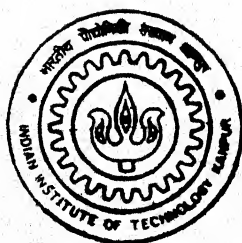


Study of Molecularly Different and Efficient Macroporous, Strong Base Anion Exchange Resin by Gas Phase Modification Using NO_x

By
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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

July, 1999

**Study of Molecularly Different and Efficient
Macroporous, Strong Base Anion Exchange Resin by
Gas Phase Modification Using NO_x**

**A Thesis Submitted
in Partial Fulfillment of the Requirement
for the degree of
Doctor of Philosophy**

by

Shishir Sinha

**to the
Department of Chemical Engineering
Indian Institute of Technology Kanpur
India**

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Dedicated to the Two Divine

and Holy Souls

Whose Convergence Gave Me

An Opportunity to Explore


This Beautiful World

My

Parents...

CERTIFICATE

This is to certify that the thesis entitled , “**Study of Molecularly Different and Efficient Macroporous, Strong Base Anion Exchange Resin by Gas Phase Modification Using NO_x**” is the original work of Mr. Shishir Sinha carried out under my supervision, and has not been submitted elsewhere for a degree.



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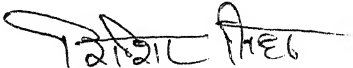
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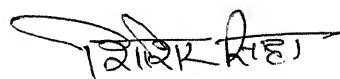


Shishir Sinha

STATEMENT

I hereby declare that the matter embodied in the thesis “**Study of Molecularly Different and Efficient Macroporous, Strong Base Anion Exchange Resin by Gas Phase Modification Using NO_x**” is the result of investigation carried out by me in the Department of Chemical Engineering, Indian Institute of Technology, Kanpur, under the supervision of Professor Anil Kumar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



Shishir Sinha

Kanpur

Dated:

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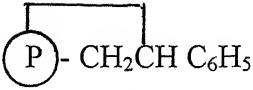
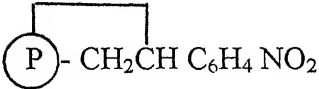
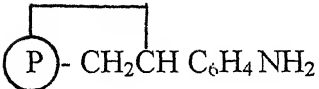

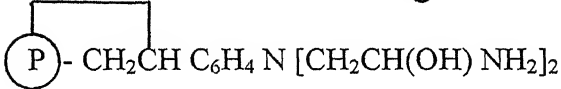
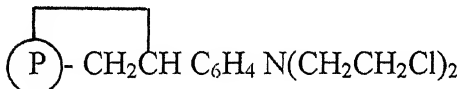


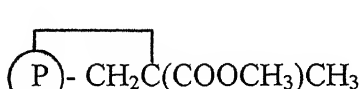
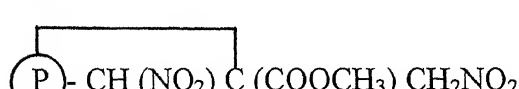
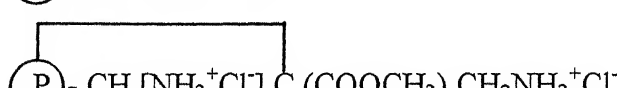
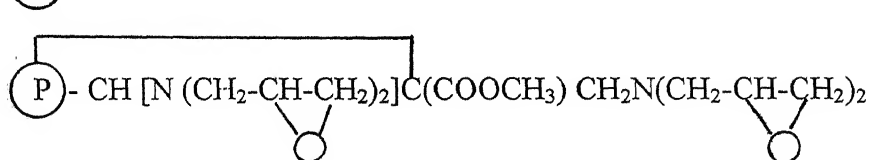
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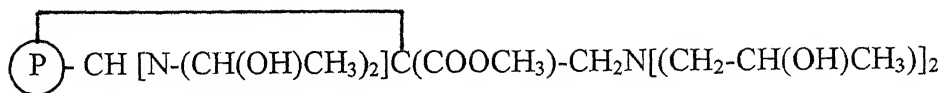
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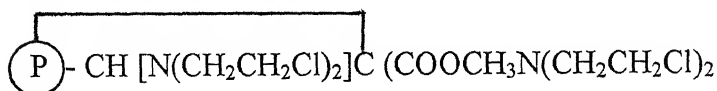
List of Symbols for Different Modifications of Resin and their Molecular Structure

- R-1  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_5$
- R-2  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{NO}_2$
- R-3  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{NH}_2$
- R-4  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{NH}_3^+ \text{Cl}^-$
- R-5  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{N} [\text{CH}_2 - \text{CH} - \text{CH}_2]_2$
- R-6  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{N} [\text{CH}_2\text{CH}(\text{OH}) \text{NH}_2]_2$
- R-7  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2$
- R-8  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{N}[\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Cl}^-]_2$
- R-9  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{N}[\text{CH}_2\text{CH}_2\text{N}^+(\text{C}_2\text{H}_5)_3 \text{Cl}^-]_2$
- R-10  $\text{P} - \text{CH}_2\text{CH C}_6\text{H}_4 \text{N} [\text{CH}_2\text{CH}_2\text{P}^+ (\text{C}_6\text{H}_5) \text{Cl}^-]_2$
- R-11  $\text{P} - \text{CH}_2\text{C}(\text{COOCH}_3)\text{CH}_3$
- R-12  $\text{P} - \text{CH}(\text{NO}_2) \text{C}(\text{COOCH}_3) \text{CH}_2\text{NO}_2$
- R-13  $\text{P} - \text{CH}(\text{NH}_2) \text{C}(\text{COOCH}_3) \text{CH}_2\text{NH}_2$
- R-14  $\text{P} - \text{CH} [\text{NH}_3^+ \text{Cl}^-] \text{C}(\text{COOCH}_3) \text{CH}_2\text{NH}_3^+ \text{Cl}^-$
- R-15  $\text{P} - \text{CH} [\text{N} (\text{CH}_2 - \text{CH} - \text{CH}_2)_2] \text{C}(\text{COOCH}_3) \text{CH}_2\text{N}(\text{CH}_2 - \text{CH} - \text{CH}_2)_2$

R-16



R-17



R-18



R-19



R-20



Chapter 1

Introduction

1.1 Literature Search

There are several class of problems in which the surfaces of the solid material are important. As an example of this is heterogeneous catalysis where the salts of catalyzing metals (Vanadium, Cobalt etc.) are either adsorbed or chemisorbed on the surfaces^{1,2} of the support. In catalytic reactions, the reactants diffuse to the surface and undergo a chemical reaction involving these adsorbed metals to form the product. In view of weak bonding of metals with its support, during these reactions there is a tendency for metals to leach out. In recent developments on catalysis, there has been an effort to modify the surfaces of the supports by generating suitable functional groups.³⁻⁶ These groups form reactive complexes with metals which does not allow leaching of metals as well as catalyze the reactions.

In another class of problems, all structural materials involve joints which are held together either using clamps or by properly designing suitable adhesive which cause the adhesion of the surfaces. These adhesive materials have normally low molecular weight polymer which can partially penetrate the surfaces to be joined and undergo suitable crosslinking reactions. The glass transition temperature (T_g), as a result of this, increases and the material become hard and solidous this way joining the structural elements. In recent applications it is desired these polymeric materials also undergo a chemical reactions with the surfaces so that the joints are held together by covalent bonding with the adhesive materials.⁷⁻¹¹

Yet another application where surfaces play an important role is in separation technology. The material to be separated may be present in the liquid or gas phase in small or large concentrations. It may be desirable to reduce this concentration to very low value (for example part per million or billion for nuclear wastes). For this purpose, it is desired to use solid absorbers having functional groups on their surfaces that would complex with the waste. Commonly available solid material belonging to this class is ion exchangers which are described below.

Commercially available strong base anion exchange resins have macroporous copolymers of styrene and divinyl benzene as their matrix. On their surfaces and within their internal pores, there are exchanging sites of quaternary trimethyl (a triethyl) ammonium groups which can under repeated exchange reaction to give necessary separation. The standard procedure of preparing these resins consists of first preparation of the copolymer macroporous resin beads by suspension polymerization and then carrying out their surface modification using chloromethyl methyl ether (CMME). This gives chloromethyl groups on their surfaces (outside and within their pores) and the strong base exchange groups are created by reacting these with trimethyl (or triethyl) amines. In this thesis, we have produced exchange resin which has chloroethyl functional groups on their surfaces instead of the usual chloromethyl groups and show that largely because of this molecular change increases the exchange capacity is enhanced by a factor of about five compared to normally available anion exchange resin.

1.1.1 Ion Exchange Resins: Ion exchange materials are insoluble solid materials which carry exchangeable cations or anions or both.¹²⁻¹⁴ Materials having exchangeable cations are cation exchangers, those having exchangeable anions are anion exchangers and those having both are called amphoteric exchangers. These materials have a porous framework, held together by lattice with labile functional groups that can be exchanged. Some of the important commercially available ion exchange resins are given in Table 1.1 and 1.2. There are naturally available aluminosilicates with ion exchange properties and these are commonly called zeolites. These are relatively soft materials, and in recent years several synthetic zeolites (sometimes called molecular sieves) have been developed and are available commercially.

Among all exchangers, the most important are organic ion exchangers, which are crosslinked polymeric gels. When the polymer matrix carries ions like $-\text{SO}_3^{-1}$, $-\text{COO}^{-1}$, PO_3^{-2} etc. it is called cation exchanger and when it has $-\text{NH}_4^{+1}$, $>\text{NH}_2^{+}$, $>\text{N}^{+}<$, $-\text{S}^{+}$ etc, it is called anion exchanger. The organic material most commonly in use is a copolymer gel of styrene and divinyl benzene (DVB) and the general purpose resin contains about 8-12% of the latter. As the DVB content is reduced, the degree of crosslinking reduces and at around 0.25% DVB, the polymeric gel swells strongly to give soft gelatinous material. As opposed to this, as DVB is increased, (at about 25%) the polymer swells negligibly and is a mechanically tough material.

The copolymer beads of ion exchange resins are prepared by suspension polymerization scheme^{12,15}. In this technique, monomers styrene and divinyl benzene are mixed with a suitable initiator like benzoyl peroxide and suspended in water under

constant stirring. This produces small droplets which are prevented from coagulation by dissolving a suspension stabilizer (like gelatin, polyvinyl alcohol, sodium oleate, magnesium silicate) in water. The particle size of the resin depends upon several factors, in particular it depends upon the choice of the suspension stabilizer. Normally a bead size of 0.1 to 0.5mm is preferred. Solvents like dodecane and amyl alcohol are known to mix with styrene and divinyl benzene in all proportion. However, if polymerization is carried out in presence of these solvents, the polymer chains precipitate because of their limited solubility. When such a system is subjected to suspension polymerization, the process of beads formation is complicated due to precipitation and the polymer chains are highly entangled. Each resin particle, has large pores filled with the solvent. Unlike macroporous particles, these are opaque and retain their size and shape even when diluent is removed. These are called macroreticular resin and will absorb any solvent filling its voids.

In one of the studies reported, polymer particles have been formed by emulsion polymerization of two tetra functional monomers in the presence of a diluent mixture consisting of a mixture of n-decanol and toluene. One of these monomer was divinylbenzene and the other synthesized by the reaction between methacrylic acid and p,p' dihydroxyldiphenylpropane diglycidylether.¹⁶ In another study¹⁷ macroporous beads containing N-Vinyl-terbutyl carbamate (NVTBC) as the main component and styrene, methyl-methacrylate or methacrylic acid as comonomer have been prepared by suspension polymerization using divinylbenzene or ethylene glycol dimethacrylate as the crosslinking agent. In this study heptane was used as porogenic agent and the beads were characterized by chemical composition and the extent of solvolysis. Macroporous

crosslinked polyacrolin-styrene-divinylbenzene resin¹⁸ was synthesized by suspension polymerization in which a solution of acrolein, divinylbenzene, styrene, toluene and benzoyl peroxide (as initiator) were prepared and mixed with a solution of sodium chloride and polyvinyl alcohol (which acts as stabilizer) in water along with subsequent heating and stirring. The monomer conversion was found to be 74.5% and the Poly(acrylonitrile-co-vinylbenzene) beads¹⁹ were synthesized with the macroporous morphology by suspension polymerization. The use of dichloroethane was studied as a solvating diluent in this copolymer resin.

In another study²⁰, styrene/acrylonitrile copolymer, styrene/acrylamide copolymer, styrene/vinylimidazole copolymer resin having fine particle were prepared by copolymerizing styrene with functional monomers such as acrylonitrile, acrylamide, N-vinylimidazole and divinylbenzene by emulsifier free emulsion polymerization using potassium persulfate or 2,2-azobis-amidinopropane hydrochloride as initiator. The size of particle obtained were in the ranges of 300-350nm in diameter, were essentially monodispersed in size and were used for immobilization of ultrafine metal particles. High density polymeric material²¹ was prepared with the styrene-divinylbenzene copolymer using the technique of suspension polymerization in heptane. The authors studied the phase separation behaviour of divinylbenzene crosslinked polystyrene from heptane and the expansion and retraction of crosslinked polystyrene. Bifunctional ion-exchange resins²² were synthesized using vinyl benzyl chloride-styrene copolymer. Copolymer of vinyl benzyl chloride, styrene and divinylbenzene were prepared by suspension polymerization at various monomer ratios with 0.5% benzyl peroxide as initiator.

Coutinho et.al.²³ prepared copolymer crosslinked beads by suspension polymerization in presence of pure di(2-ethyl hexyl phosphoric acid) (EHEHPA) in a mixture with isooctane, heptane or toluene. These copolymeric resins are best applied in the separation of rare earths by extraction chromatography. Particle²⁴ size control was studied in suspension copolymerization of styrene, chloromethylstyrene and divinylbenzene. The suspension copolymers were prepared with gelatin and poly(diallyldimethylammonium chloride) as suspension stabilizers. The influence of experimental parameters like relative amount of monomer, stirring speed and presence or absence of anionic surfactant were studied. The anionic surfactant used in this study was sodium dodecylbenzene sulfonate. Nonswellable and swellable²⁵ poly (ethylenglycol dimethacrylate) based microbeads that could react directly with the biological molecules were produced by suspension polymerization procedure. A solution of Ethyleneglycol dimethacrylate (EDMA), glycidyl methacrylate (GMA) and benzoyl peroxide was mixed with water as an aqueous suspension medium and poly(vinyl alcohol) served as a stabilizer. The copolymerization provided nonswellable, transparent, and spherical copolymer microbeads. On the other hand, swellable copolymer microbeads in the aqueous medium were obtained by using toluene as a diluent in the same copolymerization recipe.

The staged templated suspension polymerization²⁶ was used for the preparation of beads from styrene and several substituted styrene monomers, including 4-methylstyrene, 4-aminostyrene, 3-aminostyrene 4-acetoxystyrene, and 4-tert-butoxycarbonyl oxystyrene, with divinylbenzene as crosslinking agent in the presence of various amount of linear polystyrene and dibutyl phthalate as porogen. The nature of the

monomer as well as the total percentage of porogenic compounds in the polymerization mixture have considerable effect on the porous properties and surface properties of monodispersed beads. It was found that the beads with large pores can only be obtained once the percentage of porogen in the mixture exceeds a threshold value which varies with the type of monomers involved in the polymerization. Monodispersed²⁷ polymethacrylonitrile beads of varied size and crosslinked density were prepared by emulsion copolymerization of methacrylonitrile and allylmethacrylate in the absence of emulsifier. The particle size was found to be dependent upon the polymerization temperature and initiator concentration. The highest conversion polymer supported²⁸ imidazoles were prepared by copolymerization of vinyl monomers containing imidazole moiety, styrene and divinylbenzene with AIBN initiator. The resulting polymers catalyzed the reaction of octyl bromide with potassium thiocyanate and the alkylation of an active methylene compound, benzyl cyanide, under phase transfer conditions. These polymer beads have enormous use in synthesis of protein in which these beads are used as a support for different reagents.

In a study²⁹ the influence of alkali (KOH, NH_4OH , ethanolamine) was studied in the alkali treatment on the formation of multihollow structure within submicronized styrene-methacrylate acid copolymer particles. In the preparation of multihollow particles by this method it was shown that the three kinds of alkali has small influence upon the formation of multi hollow structure. Porous resin³⁰ have also been prepared by suspension polymerization of acrylic monomers and divinylbenzene in the presence of a porogen. The porosity varies greatly with the polymer composition, with the amount and type of porogen and with the condition for the preparation. The enzyme binding capacity

and activity has been determined for lipase enzyme and the best results are found for crosslinked poly (methyl methacrylate) beads while other polyacrylates are less effective. It is found that composition based on poly (methacrylic acid) are not suitable for enzyme binding.

Suitable choice³¹ of monomer/nonsolvent and monomer plus solvent/nonsolvent ratios affords a very simple method for the synthesis of functionalized crosslinked polymers suitable as polymeric supports in a wide variety of applications. The method involves an initially homogeneous solution polymerization which, because of the presence of non solvents ultimately produces insoluble particulate resin. Advantages of this procedure over the usual suspension polymerization processes include the absence of stabilizers and emulsifying agents and complete utilization of water soluble or water insoluble monomer or mixture of the two.

The classical application of ion exchange resin has been in the treatment of water for boilers and the mathematical analysis of the column has now been standardized¹⁴. It is suggested that a packed bed of these resins are first prepared and the water to be processed is pumped through it. Since ion exchange resin particles are small, the resistance to the flow of water through the column is high. It would be desirable to add these particles into vessel containing impure water and the former would absorb the impurities^{32,33}. The other known application of anion exchange resins are milk softening (substituting Na^+ for Ca^{++} of milk); removal of ion from wine and hydrochloric acid; purification of water soluble nonelectrolytes such as glycerol, glycol, sugar, formaldehyde; recovery of valuable metals from waste by chelation; recovery of nicotine

from tobacco drier gases; in nuclear industry for processing highly radioactive spent fuels, treatment of radioactive waste and purification of reactor water; as a heterogeneous catalyst in various organic reactions.

Since ion exchange particles are small, their final separation from water is difficult and to overcome this handling difficulty, the exchangeable groups are sometimes attached to magnetic particles such as iron oxide. These particles are trapped in polyvinyl alcohol crosslinked by dialdehyde (say glutaraldehyde). These resin beads are mixed with the water to be purified and after the exchange of ion has occurred, these are collected by bringing an external magnet. The bead material is highly porous, but it has the disadvantage of exchanged salt clogging the holes, this way giving reduced capacity to exchange. The alternative approach that has been adopted is to first prepare a nonporous resin of polyvinyl alcohol crosslinked with a dialdehyde. A redox initiating system is subsequently used to prepare grafts of copolymer of acrylic acid and acrylamide and the resultant material is sometimes known as whisker resin.

Most anion exchangers^{12,34} are prepared by chloromethylation of the polystyrene divinyl benzene (PS-DVB) resin which undergo subsequent chemical reaction with ammonia, primary, secondary or tertiary alkyl amines. The reaction of the chloromethylated resin with ammonia or with primary or secondary amines leads to weak base resin with amine, primary or secondary groups respectively. The reaction with a tertiary amine yields a strong base resin with quaternary ammonium groups and in a study¹² strong base anion exchange resins with quaternary phosphonium groups have

been obtained by the reaction of chloromethylated polymer with tris-dialkylamino phosphine.

Weak base groups¹² can also be introduced into crosslinked polystyrene by nitration using nitric acid and subsequent reduction of the NO₂ groups. Resins of this type carry amino groups directly attached to the phenyl rings, have very low base strengths and cannot be regenerated using the usual ASTM procedure (it has been described in Chapter 2). They have little practical importance, except as intermediates in the preparation of more specialized resins with particular groups. In a study, anion exchangers¹² have been made from acrylic and methacrylic acid by polymerization in the presence of polyamines and by treatment of crosslinked polymeric esters with polyamides. The liquid phase nitration using nitric acid degrades the resin and it loses its mechanical strength. The gas phase nitration of aliphatic and aromatic compounds using NO₂ requires high temperature (above 400°C) and have not been reported for polymeric resins^{35,36}. In a recent study the NO₂ gas has been used for degrading polymers but this occurs at high temperature (170°C) as well as pressures (4000 psig)³⁷. Several studies have also been reported on the catalytic reduction of NO₂ using zeolites and these suggest the formation of isocyanates groups on the catalyst surfaces.³⁸⁻⁵¹

Anion exchange cellulose⁵² were prepared by treating cellulose poly (glycidyl methacrylate) graft copolymer (CPGMA) with ammonia, ethylamine, diethylamine and triethylamine. Factors affecting the reactions such as duration of reaction temperature, liquor ratio, pH and the aminating agent/epoxide under ratio were studied. The anion exchange cellulose were prepared and was characterized by its capacity, potentiometric

titration and the durability of its usage. In another study⁵³, copolymerization of glycidyl methacrylate, dimethylamino ethyl methacrylate and acrylic acid with cotton fabric was carried out. Cellulose thiocarbonate-hydrogen peroxide redox initiator was used the study included the effect of the nature and concentration of the initiator and monomer, polymerization time and temperature and the liquor ratio. It was found that the percent of polymer grafted was generally favoured by increasing monomer and concentration of H_2O_2 initiator as well as the duration and the temperature of the polymerization and increased by decreasing liquor ratio.

The synthesis of cation exchanger reaction of polyglycidyl methacrylate (GMA) grafted on cellulose with hexamethyletramine initiator has been reported. The cellulose materials as crop residues as ion exchange materials⁵⁴ have been tested. Two crop byproducts, hull and sugar beet fiber, was found to have cation-exchange capacity and stability upon treatment with epichlorohydrin and NaOH. The exchange capacity and the physical stability were determined by measuring calcium binding and aqueous extraction respectively. The most economical and efficacious reaction condition were optimized and the resultant crosslinked materials had cation-exchange capacities of approximately 1 to 3 meq/g dry weight. Ion exchangers were also prepared⁵⁵ from bagasse by crosslinking it with epichlorohydrin- NH_2 or epichlorohydrin-Imidazole. This was characterized in terms of yield, anion-exchange capacity, packed volume and dye-binding properties. It was found that the highest yield occurred when 3:1 epichlorohydrin to NH_4OH molar ratio was used and this produced weak anion exchangers. A 3:1 epichlorohydrin to imidazole molar ratio was proved to be the best for making anion exchanges from bagasse.

Bifunctional ion exchange resins⁵⁶ were synthesized from vinylbenzyl chloride-styrene copolymers resins. The two types of functional groups were introduced by an Arbuzov reaction followed by sulfonation. The effect of ligand ratios, macroporosity and the matrix rigidity on the complexation of Eu (III) from solution of low pH was quantified. It was found that ion complexation kinetics and selectivity were maximized with resins having both sulfonic and phosphonic acid ligands. Maximum metal ion complexation rates depended on the balance between chemical interactions (i.e. a bifunctional network interacting with a given substrate through an access and a recognition mechanism) and physical parameters. Styrene-co-acrylonitrile resin⁵⁷ modification of PVC/CPE blends have also been studied. The effects of styrene-co-acrylonitrile resin (AS) on the mechanical properties, morphology and plasticizing and rheological behaviour of poly(vinyl Chloride)/(Chlorinated polyethylene (PVC/CPE) blends were studied. It was found that the impact strength and the tensile strength were all increased and the plasticizing and rheological behaviour were found to be improved when a certain amount of AS was added to blends.

Strongly basic anion exchange⁵⁸ resins are prepared by different monomers. First chloromethylstyrene-ethylene glycol dimethacrylate (EGDMA) copolymer beads and dimethylaminomethyl styrene-EGDMA copolymer were synthesized by suspension polymerization. The chemical and physical properties of these quaternized resins were found to be same. These resins served as conventional anion exchange resins for small organic anions, but possessed different retention for large molecular anions. It is reported that the chemical and physical structures on the external surfaces of ion exchangers are

very important. A new⁵⁹ anion exchange resin has been prepared by reacting poly (vinyl alcohol) (PVOH), as a substrate, with a mixture of triethanolamine hydrochloride, as a reactive additive bearing tertiary amine groups and as an acid liberating salt, along with a melamine formaldehyde precondensate, as a crosslinking, reinforcing and binding agent. Factors affecting the extent of reaction are time, temperature as well as molar ratios and these have completely studied. Amine content of anion exchange resin was found to be 1.17meq/gm and it has been characterized for its strength as well as durability. This weak base anion exchanger has a strength PK of 8.64 and the loss in capacity during the first five cycles is reported to 1%.

For separation of metals^{10,60-64}, organic reagents are used which form a complex with them ultimately precipitating from the solution. These are called chelating agents and it is well known that their properties are because of the functional groups. These groups can be generated on the resin through following.

- (i) polymerization of functional monomers
- (ii) grafting of second functional monomers on already prepared polymer, followed by second stage polymerization
- (iii) immobilization of chelating organic reagents onto polymer and
- (iv) polymerization of a non functional monomers followed by modification.

Preparation of chelating resins is still an area of active research and cannot be discussed in full detail in the limited scope of this chapter.

1.1.2 Supported Catalyst: Extensive work has been carried out in the field of polymer supported catalysts⁶⁵⁻⁷⁷. In a study⁶⁵ copolymer supported lanthanide complexes were synthesized and characterized. The catalytic behaviour of the complexes was studied for polymerization of butadiene and the authors reported that the activity of various individual lanthanide elements were significantly different from one another. They reported Neodymium shows the highest activity while Europium, Samarium and other heavy elements exhibit very low or no activities. A series⁶⁶ of poly (styrene-acrylamide)(PSAC) supported neodymium complexes with different content of Nd were synthesized. The relationship between the sequence distribution of the monomeric units in the PSAC and the catalytic activity of complex was investigated. It was reported that the Nd supported PSAC had optimum catalytic activity only when the distribution of short sequence of acrylamide units (n equals to 1) and long sequences of styrene units (n greater than equivalent to 25) were both higher. Methanol⁶⁷ carboxylation in a liquid flow system was catalyzed by a polymer bound rhodium (I) complex. The copolymer support with a chelating ligand was prepared using 2-vinyl pyridine, methyl acrylate and 5 mole percent crosslinking ethene diacrylate monomers. The activity and stability of the catalyst were carefully examined and reported and was found to give stable catalyst showing 4-6 times lower intrinsic activity than that of homogeneous catalyst.

Copolymerization of ethylene and propylene⁶⁸ was carried out using $\text{VOCl}_3/\text{MgCl}_2/\text{NaY}/\text{Al}_2\text{Et}_3\text{Cl}_3$ complex support catalyst. Higher polymerization activity was reported with this catalytic system. The composition and sequence structure of copolymers was controlled by alternating the ratio of two kinds of supports, and it was shown that the NaY participated in the active species, affected the insertion of monomer

and changed the composition and sequence of copolymers. Immobilization⁶⁹ of β -galactosidase was carried out on a polymeric support. Poly(vinyl alcohol) crosslinked with para formaldehyde and natural polysaccharide-chitosan in bead form and salicylic acid-resorcinol-formaldehyde polymeric resin in powder form were used for immobilization through covalent linkage. The improvement in durability of the enzyme on immobilization was reported and it was shown that on repeated use of the immobilized enzyme, no loss in the enzyme activity was observed even after 10 batches.

For catalysis using free metals, their ultrafine particles⁷⁰ were immobilized on styrene/acrylic acid copolymer by reducing the copolymer particle metal ion complexes. It was reported that the size of particles formed by reduction of complexes was smaller than that by refluxing the metal ion solution in the presence of copolymer particles. Further, the catalytic action depended on the amount of metal ion immobilized. Studies⁷¹ were carried out on immobilized polymer-bound imidazole-copper (II) complex catalysts. The oxidative coupling polymerization of 2,6-dimethylphenol catalyzed by copper (II) complexes of poly(styrene-co-N-vinylimidazole) (Cu(II)-PS-Im) in toluene/isopropanol (13/2v/v) was investigated. It was reported that the mono complex was found to be more active catalyst for the reaction for poly (2,6-dimethyl-1,4-phenylene oxide) formation than dinuclear complexes.

Zirconium tetrabenzyl⁷² was used as the co-catalyst in olefin polymerization together with MgCl_2 -supported titanium catalyst. Propylene polymerization was performed with a $\text{MgCl}_2/\text{TiCl}_4$ catalyst containing ethyl benzoate as the internal donor with tetrabenzyl zirconium as the cocatalyst. The coordinately⁷³ unsaturated nature of tetrahedral cobalt (II) complexes significantly inhibited the thermal polymerization of

acrylamide. They imparted significant induction period during AIBN-initiated polymerization of MMA and acrylamide. Binding of noble⁷⁴ metal salt e.g. PdCl_4^{2-} to a functional ligand on a polymer surface was performed followed by reduction to its zerovalent state and subsequent reductive deposition of transition metal ions such as copper, nickel and cobalt provided a controlled zerovalent metal polymer composites. Physical as well as chemical properties of these metallized beads were discussed.

In a different study⁷⁵ polymeric coordination complexes based on cobalt, nickel, and ruthenium were prepared and their thermal properties were evaluated. A model for attachment⁷⁶ of active species on gellular polymer beads was developed. In this model equation for the equilibrium between the stresses and the degree of swelling and for the mass balance of substrate and functional group are proposed in order to analyze the attachment of active species onto gellular polymer beads. Four chelating resins⁷⁷ derived from crosslinked poly(chloromethylstyrene) (PCMS), four derived from crosslinked poly(glycidylmethacrylate)(PGMA) and one crosslinked poly(4-vinylpyridine) resin have been used to immobilize Mo complexes. The metal centre was introduced to the polymeric ligands by ligand exchange. The initially blue coloured polymers were activated by treatment with the excess tert-butylhydroperoxide to yield bright yellow resin. Each resin was then employed as a catalyst in the solution epoxidation of cyclohexene using tert-butylhydroperoxide as the oxidant at approximately 80°C. It was found that resin catalysts were highly active with the PGMA-based species due to its higher polarity and more favourable morphology.

The oxidation⁷⁸ of benzoin by polymer supported N-bromo sulphonamide in acetonitrile and in the presence of sulphuric acid has been studied. It was found that the

reaction was first order with respect to N-bromosulphonamide and hydrogen ion concentration. The rate law and a probable mechanism, involving generation of reactive bromonium ion was discussed. Polymer supported⁷⁹ 1,5,7-triazabicyclo [4,4,0]deca-5-ene (TBD) was prepared by the reaction of chloromethylated polystyrene resin which was crosslinked using 2-mole percent divinylbenzene. The reaction of benzoic acid with bromobutane was carried out in toluene or acetonitrile in the presence of polymer supported TBD or polymer supported 1,8 diazabicyclo [5,4,0] undec-7-ene (DBU). It was reported that rate of esterification was dependent on the ring substitution of the supported bases and the solvent. The reduced ring substitution resulted in the increased swellability of the polymeric beads containing benzoate or bromide ions for toluene and thereby giving increased reaction rate. It was reported that the rate with high ring substituted bases increased in acetonitrile because of high swellability of the immobilized salts. A rhodium complex⁸⁰ of bifunctionalized polystyrene was prepared and used in the hydromethylation of 1-butene. The bifunctionalized polymers contained with amino and hydroxyl groups. Polymer supported⁸¹ chiral oxazaborolidines bound to the polymer via the boron atom, have been prepared from a series of crosslinked polymer synthesized using 2-vinylthiophene. The polymer supported oxazaborolidines were used to catalyse the reduction of prochiral ketones using the boranedimethyl sulfide complex, a reduction which also occurs in the absence of catalyst to give a racemic products.

Synthesis⁸² of several polymer supported palladium catalysts has been carried out and their catalytic behaviour for selective hydrogenation of mesityl acetone was studied. In this study, styrene-divinylbenzene copolymer bead was first prepared and after the chloromethylation of the resin and amination, five kinds of polymeric amines were

obtained. These polymers were reacted with palladium chloride and then reduced. These synthesized catalysts were then used to catalyze the selective hydrogenation of mesityl acetone using methanol as a solvent. Two new polymer⁸³ containing chiral oxazaborolidines as pendant groups have been prepared by chemical modification of crosslinked 2-vinylthiophene copolymers. The polymers were used as chiral auxiliaries in the catalysis of asymmetric addition of diethylzinc to aldehydes. It was found that when these catalysts were used in the alkylation of benzaldehyde obtained between 51 and 28%. The effect of reaction parameters like solvent, temperature. Amount and loading of catalyst were also discussed.

Polymer supported colloidal⁸⁴ metal catalysts were synthesized directly from monomers and metallic precursor in one step. Different surface characterization techniques like ESCA, SEM and IR were used to access the structure of the polymer catalysts and the distribution and dispersion of metal on its surface. The influence of the synthetic condition on the structures of the catalyst was studied. In another study⁸⁵ the catalytic properties in the hydrogenation of olefins and the stability of polymer supported colloidal palladium catalysts prepared by one step preparation method has been investigated. A comparison of catalytic properties and comparison of polymer supported and SiO₂ supported palladium catalyst has been made. It was reported that the polymer catalyst possessed high catalytic activity for hydrogenation of olefins with low metal loss having good stability.

In an alternate study⁸⁶ poly(styrene-co-acrylamide) titanium complexes were prepared and characterized. It was found that the coordination number of acrylamide (A_m) to titanium in the complexes is strongly dependent on A_m content in the

poly(styrene-co-acrylamide) but not on the Am/Ti ration in the feed. The catalytic activity of complexes was studied and it was reported that the catalytic activity was greatly affected by the Am/Ti ration in the complexes. In one of the study⁸⁷ several functional polystyrene supported metal (Ru, Rh, Pd) catalysts were synthesized. The hydrogenation selectivity of these catalysts for polyunsaturated cycloolefines (1,5,9-cyclododecatriene, cyclopentadiene) and unsaturated carbonyl compounds (mesityl oxide, crotonaldehyde acrylic aldehyde) was investigated). Some important parameters like pore size, crosslinkage of polymer supports, donor atoms were examined.

1.1.3 Modification of Polymeric Surfaces: Many properties of a material are dependent primarily on the surface structure and the on the chemical composition of the out most surface layer.⁸⁸ Wetting and coating characteristics, frictional behaviour and physiological compatibility are example of such properties. In several applications it is difficult to find a material with both appropriate bulk properties and required surface properties. It is therefore often desirable to combine the surface properties of one material with the bulk properties of another. With polymers, this can be done through surface modification, i.e. by altering the chemical structure of a thin surface layer without affecting the bulk properties of the material. Several methods for modification of polymer surfaces have been developed⁸⁸ including chemical method⁸⁹, plasma treatment⁹⁰ and grafting reactions involving UV irradiation.⁹¹

The chemical technique of surface modification is one of the most important method in which organical reactions are carried and between functional groups of surfaces and organic reagents. Surface modification⁹² of poly(p-phenylene terephthalamide, PPTA) film is carried out with 2-amino ethanethiol (AET) to adhere to

silicon rubber. This is an effective surface modification of PPTA film. The X-ray photoelectron spectroscopy analysis show that the AET treatment does generate oxygen functionalities at the surface of the PPTA. In the AET treatment process, a part of the amide group near the surface of the PPTA film is hydrolized to form carboxylic acid groups and amino groups. The oxygen functionalities are condensed at the film surface and the nitrogen functionality is diluted at the film surface. A method⁹³ has been suggested to generate a porous region near the surface of a polymer in which the region near the surface is swollen by immersing the polymer for a short time in a solvent (chloroform). Subsequently, the polymer is dipped in a nonsolvent (for the polymer) but is miscible with the solvent. The formation of the porous region is a result of the swelling accompanied by disentanglement of the surface molecular chains. This occurs because some of them dissolve during the immersion in the solvent and then there is rapid extraction of the solvent from the swollen region by the nonsolvent. The porous surface provides a matrix into which a second incompatible monomer can be polymerized.

In a study⁹⁴, the effect of solvent on the accessibility and reactivity of an ester-bound fluorophore at a functionalized polyethylene-solvent interface have been examined. Fluorophore-labeled polyethylene surface are prepared by blending together a small amount of a pyrene ester-terminated ethylene oligomer and a host linear low density polyethylene in solution. Film cast from such solutions have then been studied by fluorescence spectroscopy to show that a significant number of entrapped pyrene groups are at the polyethylene solvent interface and are capable of reaction with soluble reagents. The immunoreactivity⁹⁵ of the resin antibodies has been studied fax resins

having polystyrene have been studied as a function of the chemical treatments used to prepare the polystyrene surface. Injection molded polystyrene beads are nitrated with sulfuric and nitric acids followed by reduction to form amine groups. The nitration conditions used affect the quantity of nitro and amino group introduced, and ultimately the quantity of antibody coupled to the surface. Aminated resins are also grafted with monomethoxypolyethylene glycol prior to antibody coupling to determine if this modification could lower non-specific protein binding to the beads. Using the wet chemistry technique⁹⁶, the surface of the poly (aryl ether ether ketone) (PEEK) film (PEK-OH), and covalently bond hexamethylene diisocyanate is reacted by addition onto the hydroxyl functions. The resulting PEEK-NCO film displayed free isocyanate terminal groups and its hydrolysis gives the PEEK-NH₂ film in high 85% extent of derivation.

The surface of poly(p-phenylene terephthalamide)⁹⁷ (PPTA) film has also been modified by oxygen plasma and the modified film surface analysed by an advancing contact meter and the x-ray photoelectron spectroscopy (XPS). The advancing contact measurement showed that the oxygen plasma treatment made the surface of the PPTA film hydrophilic. The XPS analysis confirmed on increase in the O/C and the N/C atom ratio, especially the O/C atom ratio at the PPTA film surface by the oxygen plasma treatment. The analysis suggested the formation of carboxylic acid group as well as protonated amino group and the formation of the oxygen and the nitrogen functionalities formed by the oxygen plasma treatment is not restricted to the surface of the PPTA film alone but penetrates inside. Some biodegradable⁹⁸ polymers for example poly (γ -lactone) and poly(succinate) are surface treated by glow discharge plasma under appropriate

conditions and the effects have been investigated with respect to the weight loss, surface morphology change, and bio-degradation. The weight loss caused by oxidative plasmas are in general higher than those for a polyester sheet made of poly (ethylene terephthalate). After glow discharge treatments, the characteristic surface morphology measured by the scanning electron microscopy (SEM). The surface became more wettable and activated by the plasma treatment and its biodegradation investigated in composts under appropriate condition.

A radio frequency plasma⁹⁹ has been used for functionalization of the surface of polyethylene terephthalate (PET) by grafting amine functions with an NH_3 plasma. The possibility of grafting primary amine functions by ammonia plasma treatment and fixing amino acids on the aminated PET samples are shown by x-ray photoelectron spectroscopy and radiochemical assays. Surface modification¹⁰⁰ of poly(aryl ether ether ketone)(PEEK) film by oxygen plasma treatment has also been investigated. Two procedures, the direct plasma treatment and the remote oxygen plasma treatment, have been used and the efficiency of the hydrophilic modification examined. The direct and the remote oxygen plasma treatment lead to degradation of the PEEK film as well as hydrophilic surface modification. The degradation disturbs the surface modification and the remote oxygen plasma treatment has been found to be suitable for the hydrophilic surface modification of the PEEK film.

The grafting¹⁰¹ of 2,3-epoxypropyl methacrylate on polypropylene fabric is carried out by the gamma-ray preirradiation grafting technique. The grafting extent is found to be dependent on the storage condition of the irradiated polypropylene fabric, the preirradiation dose, the reaction time, the temperature and the addition of solvent used.

The 2,3 epoxypropyl methacrylate-grafted polypropylene fabric is reacted with ammonia and various types of amines for different reaction times and temperatures. The extent of amination occurred and their rate of animation, in the decreasing order, followed the order dimethyl amines, trimethyl amine, methyl amine and least for ammonia. The surfaces¹⁰² of poly (methyl methacrylate) and a UV curable acrylic lacquer have been modified by the addition of small amounts of polymerizable, monomeric surfactants and a surface-active polymer. In the system used, the surfactants concentrate at the interface towards less polar phase and addition of 1% W/W of a monomeric surfactant to an acrylic lacquer gives a surface concentration of 50% at the two interface toward air.

Among the various procedure of surface modification¹⁰³, ion beam bombardment has been used to study the effect of modification on polymer surface properties. The surfaces of polyethylene, polypropylene, polystyrene and polyimide has been bombarded with Ar^{++} and N^{++} . Common surface analytical techniques such as SIMS, XPS and AFM have been used to characterize the bombarded polymeric surfaces. The benzene ring component of the polymer plays an important role in the increase of the valence electron density and in the delocalization process of the excess charge during the ion bombardment. The changes, called the matrix effect, accompanied by the reduction of the ionization probability of hydrogen have been observed at the polymer surface. Argon plasma-penetrated¹⁰⁴ polytetrafluorethylene (PTFE) films have been subjected to surface modification by near UV light-induced graft copolymerization with acrylic acid (AAc), sodium salt of styrenesulfonic acid (NaSS) and N,N-dimethylacrylamide (OMAA). The surface composition and microstructures of the modified films have been characterized by x-ray photoelectron spectroscopy (XPS). A stratified surface microstructure with a

significantly higher ratio of the substrate to graft chain in the top surface layer than in the sub surface layer has always been obtained for PTFE surface with substantial amount of the hydrophilic graft. The graft yield has been found to increase with the time of Argon plasma pretreatment and the monomer concentration. A covalent immobilization of trypsin on the AAc polymer grafted PTFE films was facilitated by water soluble carbodiimide and the effective enzyme activity increased initially with increasing surface concentration of the grafted AAc polymer but became saturated at the moderate AAc polymer concentration.

1.1.4 Surface Modification of Membranes : Pervaporation membranes¹⁰⁵ derived from seven homo-polymers of poly (amidesulfonamide) (PASAs) were prepared by casting 10-17% polymer solutions in N,N-dimethylacetamide. The membranes were characterized by sorption experiments, scanning electron microscope and wide-angle X-ray diffraction. During the pervaporation of 90% wt. percent aqueous solution of methanol, ethanol, 1-propanol and 2-propanol all membranes were preferentially permeable to water and their separation factors were mainly dependent on the molecular weight of the solvent. Polymeric membrane based on N, N'-bis (4-amino phenyl sulfonyl)-1,3-diaiminopropane and isophthaloyl chloride exhibited the best selectivity factor of 1984 for a 10:90 (by weight) mixture of water/ethanol at 20°C. In another study¹⁰⁶ thermosensitive membranes with high mechanical strength were prepared by heterogeneous graft copolymerization of N-isopropylacrylamide (NI-PAAm) onto cellophane in a nitric acid solution using cerium ammonium nitrate initiator. Behaviour of solution such as lithium chloride and poly (ethylglycols)(PEGs) through the membrane at various temperatures was investigated. It was found that the degree of graft copolymerization of NIPAAm on

cellophane depended on temperature, time and the initiator concentration. The copolymer membranes having a high content of the NIPAAm moiety could be obtained at 25°C for 24 hours. It was observed that the permeation of Li^+ through the membranes was affected by temperature and in addition to this, the permeation rate of Li^+ decreased with an increasing amount of the NIPAAm moiety in the membranes.

The transport of pharmaceuticals¹⁰⁷ through silk fibroin membrane prepared from chinese cocoon has been reported. The permeability coefficient of five kinds of pharmaceutical 5-fluorouracil (5 FU), L(+)-ascorbic acid (Vc), resorcinol, sodium phenosulfonate (SPS) and benzyltrimethylammonium chloride (BTAC) were measured in the pH range from 3.0 to 9.0. This silk fibroin membrane was an amphoteric ion-exchange membrane and the positively charged pharmaceutical, BTAC was excluded from the membrane below the isoelectric point. On the other hand, the negatively charged SPS had a permeability that decreased as the pH increased. It was found that the neutral molecule, resorcinol penetrated through the membrane independent of the pH value over the measured pH range.

Surface modification¹⁰⁸ of acrylonitrile (PAN) copolymer membrane has been reported. In this study, the membranes of PAN containing 5-5% methyl methacrylate (MMA) and 4.0 sodium methyl propylenesulfonate were surface modified by grafting acrylamide (AAM) with ceric ammonium nitrate as initiator in the aqueous medium. It was found that the extent of grafting varied with the medium such as the amount of dimethyl formamide and Tween-20 in the reaction mass. The grafted copolymer was identified by IR and the bond energies by XPS and both spectroscopic method confirmed the ester group of MMA unit. These units on the surface of Pan membranes could also be

partially hydrolized into carboxyl group in the copolymerization. Sorption and diffusion¹⁰⁹ of ethanol, 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE) were investigated in poly dimethylsilexane (PDMS) membranes using a gravimetric technique. The thermodynamic equilibrium and kinetic properties were evaluated at temperatures of 25, 100 and 150°C. The sorption isotherms for TCA and TCE correlated well using the Flory-Huggins model. The solubility coefficients of TCA and TCE increase with activity, but it remained almost constant for ethanol, TCA and TCE sorption in PDMS decreased strongly with temperature in contrast to that found for ethanol.

1.2 Objective of Thesis : In this thesis, we propose to

- (a) study suspension polymerization of styrene divinylbenzene copolymer by varying the nature and amount of diluent (toluene) as well as gelatin (the particle size controller).
- (b) study gas phase nitration of styrene divinylbenzene copolymer resin
- (c) study the time and temperature effect of NO_x on the nitration of PS-DVB resin
- (d) carry out the amination of nitrated resin
- (e) study the effect of nitration on the capacity of aminated resin
- (f) study the regeneration ability of anion resin formed
- (g) the study the effect of modification with epichlorohydrin to the aminated PS-DVB resin in order to make the aminated resin regenerable
- (h) study the chloroethylation of aminated PS-DVB resin

- (i) study the effect of extent of nitration on the chloroethylated PS-DVB resin
- (j) study the effect of quaternization with trimethylamine, triethylamine and triphenylphosphene of chloroethylated resin
- (k) study the effect of equilibrium moisture content of PS-DVB resin
- (l) carry out the same study for the methacrylate based crosslinked polymer (PMMA-EDMA).

Table 1.1

Properties of Various Commercially available Ion Exchangers

S. No.	Resin Type	Charact ristic	Matrix Type	Counter Ion	Ionic Form	Particle Size (mm)	Moisture Content (%)	Total Exchange Capacity meq/ml	Application
1	Isoporous	Strong basic	Crosslinked Polystyrene	- N^+R_3	Cl^-	0.3-1.2	47-55	1.2	DM Application
2	Isoporous	Strong basic	Crosslinked Polystyrene	- N^+R_3	Cl^-	0.3-1.2	47-55	1.2	Used in Mixed Bed
3	Isoporous	Strong basic	Crosslinked Polystyrene	- N^+R_3	Cl^-	0.3-1.2	46-55	1.2	DM Application
4	Macroporous	Strong basic	Crosslinked Polystyrene	- N^+R_3	Cl^-	0.3-1.2	50-56	1.1	Dem mineralizing of Water
5	Macroporous	Strong basic	Crosslinked Polystyrene	- N^+R_3	Cl^-	0.3-1.2	47-54	1.1	Dem mineralizing of Water
6	Macroporous	Strong basic	Crosslinked Polystyrene	- N^+R_3	Cl^-	0.3-1.2	52-56	0.9	Removal of Colour
7	Isoporous	Weakly Basic	Crosslinked Polystyrene	- N^+R_2	Cl^-	0.3-1.2	46-55	1.1	Ion Exchanger for DM
8	Macroporous	Weakly Basic	Crosslinked Polystyrene	- N^+R_3	Free Base	0.3-1.2	47-55	1.5	Removal of Strong Acid from water
9	Macroporous	Weakly Basic	Crosslinked Polystyrene	- N^+R_2H	Free Base	0.3-1.2	52-56	1.4	Treatment for non aqueous soln
10	Macroporous	Weakly Basic	Crosslinked Polystyrene	- N^+R_2H	Free Base	0.3-1.2	47-55	1.3	High Capacity Weak base resin
11	Macroporous	Weakly Basic	Crosslinked Polystyrene	- N^+R_2H	Free Base	0.3-1.2	52-56	1.6	High Capacity Weak base Resin
12	Macroporous	Weakly Basic	Crosslinked Polystyrene	- N^+R_2H	Free Base	0.3-1.2	47-55	1.4	Deacidification of glyoxal

Table 1.2
Properties of Various Commercially Available Cation Exchangers

S. No.	Resin Type	Charact ristic	Matrix Type	Counter Ion	Ionic Form	Particle Size (mm)	Moisture Content (%)	Total Exchange Capacity meq/ml	Application
1	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	Na ⁺	0.3-1.2	54-60	1.8	Water Softening
2	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.3-1.2	54-60	1.8	
3	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	Na ⁺	0.3-1.2	47-54	2.0	Water Softening, dealkalising
4	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.3-1.2	47-54	2.0	
5	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.3-1.2	47-54	2.0	Use in mixed bed
6	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.3-1.2	44-49	2.0	Use in layered bed
7	Gel	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.35-1.2	44-49	2.0	Use in layered bed
8	Macroporous	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.35-1.2	50-56	2.0	Condensate polishing
9	Macroporous	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.3-1.2	50-56	2.0	For non-water application
10	Macroporous	Strongly Acidic	Styrene DVB	-SO ₃ ⁻	H ⁺	0.3-1.2	50-56	2.0	Deionisation of sugar syrops
11	Gel	Weakly Acidic	Crosslinked Acrylic	-COO ⁻	H ⁺	0.3-1.2	46-54	4.0	For removal of alkalinity in water
12	Gel	Weakly Acidic	Crosslinked Acrylic	-COO ⁻	H ⁺	0.3-1.2	50(min)	3.5	Removal of Vitamin B ₁₂

Table 1.3

Properties of Various Anion Exchangers Developed during the Study

S.No.	Resin Type	Charac- teristic	Matrix Type	Counter Ion	Ionic Form	Particle Size (mm)	Moisture Content (%)	Total Exchange Capacity meq/ml	Application
1	Macroporous PS-DVB-NH ₂	Weak Base	Crosslinked Styrene-DVB	- N ⁺ H ₃	Cl ⁻	1.0	27-53	1.42	Non Regenerable
2	Macroporous PS-DVB-EPH	Strong Base	Crosslinked Styrene-DVB	-CH ₂ -CH-CH ₂ - N ⁺ H ₃ OH	Cl ⁻	1.0	36-57	2.88	Regenerable
3	Macroporous PS-DVB-DCE- TMA	Strong Base	Crosslinked Styrene-DVB	-CH ₂ -CH ₂ -N ⁺ (CH ₃) ₃	Cl ⁻	1.0	21-41	4.90	Regenerable
4	Macroporous PS-DVB-DCE- TEA	Strong Base	Crosslinked Styrene-DVB	-CH ₂ CH ₂ N ⁺ (C ₂ H ₅) ₃	Cl ⁻	1.0	9-37	5.14	Regenerable
5	Macroporous PS-DVB-DCE- TTP	Strong Base	Crosslinked Styrene-DVB	-CH ₂ CH ₂ P ⁺ (C ₆ H ₅) ₃	Cl ⁻	1.0	35-50	5.16	Regenerable
6	Macroporous PMMA-EDMA	Weak Base	Crosslinked MMA-EDMA	- N ⁺ H ₃	Cl ⁻	1.0	36-50	4.86	Regenerable
7	Macroporous PMMA-EDMA- EPH	Weak Base	Crosslinked MMA-EDMA	-CH ₂ -CH-CH ₂ - N ⁺ H ₃ OH	Cl ⁻	1.0	32-51	2.94	Regenerable
8	Macroporous PMMA-EDMA- DCE-TMA	Strong Base	Crosslinked MMA-EDMA	-CH ₂ -CH ₂ -N ⁺ (CH ₃) ₃	Cl ⁻	1.0	25-51	3.34	Regenerable
9	Macroporous PMMA-EDMA- DCE-TEA	Strong Base	Crosslinked MMA-EDMA	-CH ₂ -CH ₂ -N ⁺ (C ₂ H ₅) ₃	Cl ⁻	1.0	25-54	4.35	Regenerable
10	Macroporous PMMA-EDMA- DCE-TTP	Strong Base	Crosslinked MMA-EDMA	-CH ₂ -CH ₂ -P ⁺ (C ₆ H ₅) ₃	Cl ⁻	1.0	30-55	4.20	Regenerable

An Efficient Technique for Gas Phase Nitration of PS-DVB Resins using NO_x

2.1 Introduction

Ion Exchangers are insoluble solid material that carry either chelating functional groups, cations or anions or all three of them. Among all these the most important are organic exchangers which are crosslinked polymer gels. The properties of these arise because of the functional groups on the polymer and these are created on the polymer gel by chemical reactions. These could be obtained by (a) polymerizing functional monomers (b) grafting of second functional monomer on already prepared polymer, followed by second stage polymerization (c) immobilizing suitable organic reagents and (d) polymerizing nonfunctional monomers followed by their modification. The organic material most commonly in use is a copolymer gel of styrene and divinylbenzene (denoted by PS-DVB) and the general purpose resin contains about 8-25% of the latter.

The PS-DVB copolymer resin is preferred because of the fact that these have preponderance of phenyl rings on the network which can be easily functionalized. In chapter 1 we have presented a literature search on the preparation of crosslinked resin, their functionalization by chemical modification and their use as ion exchange resin and membrane separation. All functionalizing reactions reported are found to be liquid phase reactions in which penetration of reagents into the resin is extremely important. The common starting point of these reactions appears to be the chloromethylation reaction in which $-\text{CH}_2\text{Cl}$ groups are generated using an extremely carcinogenic reagent chloromethyl methyl ether (CMME). The overall reaction is not

efficient and about 1-2% chloromethyl groups per gram of resin is all that can be obtained.

In this chapter we report a gas phase nitration of styrene divinylbenzene (PS-DVB) copolymers, using a mixture of NO and NO₂ gas (sometimes called NO_x) at relatively low temperatures and this has not been reported in literature. For the purpose of anion exchange resins, aminated resin can be easily formed by reducing these nitrated functional groups of the gel with hydrazine hydrate. The resin thus formed can also serve as a reasonable starting point for more advanced modifications. Since the modification carried out in this work is a gas phase reaction of NO_x with the copolymer resin, the availability of the reagents within the gel depends largely on how fast it can be taken up the gel. In order to assess the efficacy of this gas phase reaction, we have converted these into anion exchange resins and compared it with the commercially available resin (DOWEX, Dow Chemicals). We found that the exchange capacity of our resin to be about five times more than that of DOWEX resin indicating high efficiency of the gas phase nitration technique.

In the following, we present the conventional chloromethylation process for manufacturing anion exchangers and because formalin as one of the reactants, the waste stream is highly polluting. As opposed to this in the present nitration scheme of the PS-DVB resin by NO_x, the gas is completely consumed and in this regard represents a clean technology. We have confirmed the nitration of PS-DVB resin by FTIR and ESCA and demonstrated the presence of nitrogen in the polymer by adopting the Lassaigne spot test. In order to determine the extent of the nitration of the resin, with respect to time of nitration reaction we have aminated them by reducing the nitrate functional groups with hydrazine hydrate. We have carried out

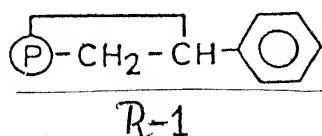
linear regression analysis on the experimental data on the consumption of NO_x and the exchange capacity in Appendix I. For this, we assumed 1st, 2nd and 3rd kinetics for both the exchange capacity and NO_x consumption data and determine the rate constants and the coefficient of correlation, r . This analysis shows that as the order of the kinetics is increased, the fit of the data of NO_x consumption versus time improves with small difference in 2nd and 3rd order kinetics. However, for the data of exchange capacity versus time, 1st order is definitely is better fit with the fit deteriorating with increasing order.

2.2 The Conventional Process:

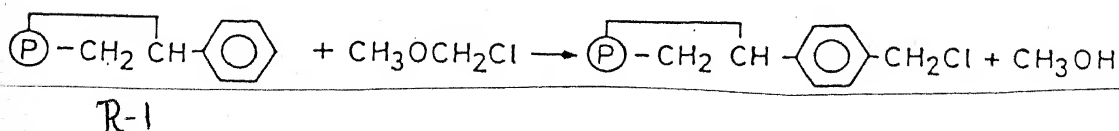
In the conventional commercial process, polystyrene-divinylbenzene resin is prepared and then chloromethylated. Thereafter the chloromethylated resin is aminated with primary, secondary (giving weak base resin) or tertiary amines³⁴ (giving strong base resin). Various steps in this process are summarized as follows:

Step 1: Chloromethylmethylether (CMME) is prepared by the reaction of methanol, 35% HCl and paraformaldehyde at 0°C for 24 hrs. After this the reaction mass separates in two layers, one of which is chloromethylmethylether in water and the another is unreacted formaldehyde which has to be discarded or reused. The CMME layer is stored at 0°C as it tends to decompose at higher temperature.

Step 2: Polystyrene-divinylbenzene copolymer resin is refluxed with CMME for 24 hrs. One repeat unit in the polymer matrix can be represented by

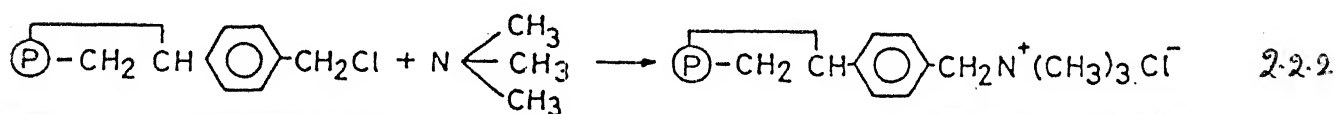


and the chemical reaction with CMME can be schematically shown by



Thereafter the resin is filtered and the filtrate comprising of a mixture of dichloromethylether and formaldehyde is discarded. The chloromethylated resin is are then washed and dried in an oven kept at 80°C.

Step 3: The chloromethylated PS-DVB resin can be quarternized with the help of tertiary amines. In this step, the chloromethylated resin is reacted with the latter at 0°C for 48 hr with intermittent shaking. After filtration, the product is washed with 0.1N NaOH and 2N HCl and the reaction¹² can be represented by



The above reaction can also be carried out with primary and secondary amines. The involvement of extremely carcinogenic CMME in the first two steps and discharge of unreacted CMME and formaldehyde makes this process non-ecofriendly. The presence of unreacted formaldehyde even in the concentration range of parts per million is known to destroy the local aquatic life. The traditional process also requires special handling because of low storing temperature (0° C) for CMME.

In the present study, a new scheme of considerably efficient gas phase nitration of PS-DVB resin has been developed. In this scheme, the gas NO_x is completely consumed and there is no side product formed along with the fact that there is less processing time and no special handling is required. In this chapter, we have prepared macroporous PS-DVB resin using suspension polymerization. We have carefully varied the reaction parameters systematically and determined their effect upon the particle size distribution. This study has lead us to determine reaction condition that would yield large particles. We have particularly separated 1mm

copolymer resin beads and used these for the nitration reaction. We have subsequently reduced the resin and found that the exchange capacity of the anion exchange resin thus prepared depends strongly upon the duration of nitration. Optimal results were found to occur for 5 hours of nitration.

It may further be pointed out that on amination in eqn.2.2.2, we generate an aniline moiety in the PS-DVB resin and these have very low pK values. As is expected, these anion exchange resins cannot be regenerated for repeated usage as commercial resins are regenerated. In view of this, in Chapter 3, we study further modification of aminated PS-DVB resins so that they could be repeatedly used in exchanging anions. The extensive experimentation of the subsequent chapter show that under certain modification, the exchange capacity of our resin becomes atleast five times that of commercial resins.

2.3 Experimental Section

2.3.1 Preparation of Macroporous Resin:

In order to get large particle PS-DVB co-polymer resins, the technique of suspension polymerization³⁴ has been used. In this study organic phase is prepared by mixing styrene (280g, 3.04g-moles) divinylbenzene (80g, 0.62g-moles) azobisisobutyronitrile (4g, 0.02g-moles), and toluene (200g, 2g-moles). This organic phase was suspended in an aqueous solution containing distilled water (900 ml), sodium sulfate (48 g, 0.034 g moles), calcium carbonate (8 g, 0.08 moles) and gelatin (0.028 g).

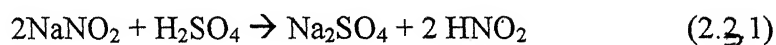
The suspension polymerization process is carried out under controlled stirring at $60 \pm 2^\circ\text{C}$ for four hours in a setup shown in Figure2.1. After this time, the temperature of the reaction mass is increased to $90 \pm 2^\circ\text{C}$ in half an hour and then it is

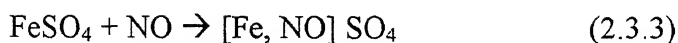
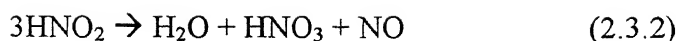
kept constant for the next two hours. The resin in the form of beads now has considerable mechanical strength and are separated and washed with water. To remove excess calcium carbonate, 0.1N HCl solution is added to the resin. Again the resin is separated, washed with water and finally with methanol and are dried in oven maintained at 70-75°C. During experimentation, gelatin content in the aqueous phase is found to play an important role in controlling the particle size of the resin and is found that the average particle size tends to decrease with the increase in gelatin content.

2.3.2 Gas Phase Nitration of PS-DVB Resin using NO_x

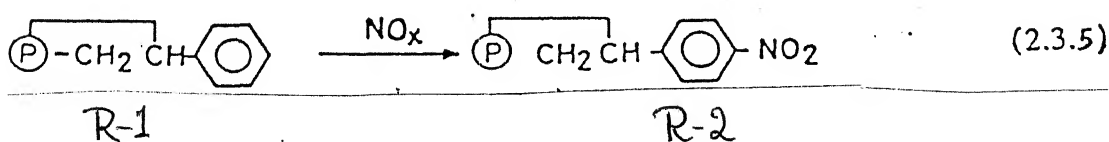
In the literature, nitration of macroporous PS-DVB copolymer has been reported to occur by reacting it with concentrated nitric acid (HNO₃)¹² which can easily be aminated using hydrazine hydrate. However due to use of concentrated HNO₃ these particle loose mechanical strength and are degraded. In addition to this the literature reports that these resins to have extremely low base strength, cannot be regenerated for repeated usage and is of no commercial significance for separation.

Direct gas phase nitration of polystyrene-divinylbenzene (PS-DVB) resin is carried out in a 2.5 liter reaction bottle shown in Figure 2.2. This reaction vessel is equipped with an aluminium cap with 1.2mm opening at the top for injecting the gas which is closed by a silicon rubber septum. Using the method of reference^{112,113} a mixture of NO and NO₂ (called NO_x) is generated in a 1.5 liter, two neck round bottom flask by reacting Sodium Nitrite NaNO₂ (10g, 0.14g-mole) with Sulfuric Acid (H₂SO₄ sp.gr.1.18, 25 ml.) in presence of Ferrous Sulfate FeSO₄ (5g, 0.072g-mole). The flask is equipped with a rubber septum for withdrawing NO_x with the help of 100 ml syringe. The generation of NO_x occurs through the following mechanism¹¹²:





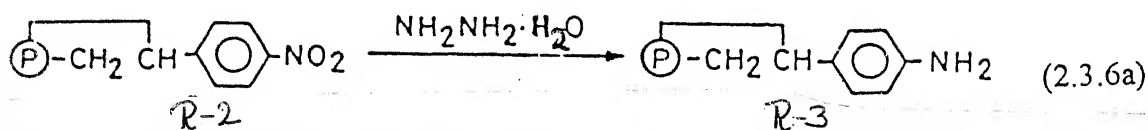
Approximately 1.5 g of PS-DVB resin is introduced into the reaction vessel and is placed in the oven maintained at the desired reaction temperature. A small needle is punctured through the silicon septum of the reactor vessel so as to allow a thermal equilibrium with the oven. The gas inside the bottle expands due to heating and escapes through the needle. After this, the needle is removed, the vessel is taken out and allowed to cool at room temperature. This creates slight vacuum inside the vessel so that when NO_x is introduced into the bottle, at the reaction temperature, the total pressure remains approximately at 1 atm. After feeding the required amount of gas mixture, the vessel is again kept into the oven maintained at the reaction temperature. After completion of nitration the vessel is taken out and allowed to cool to the room temperature for withdrawing the resin for further analysis. The product form is the nitrated resin and its formation can be represented by.



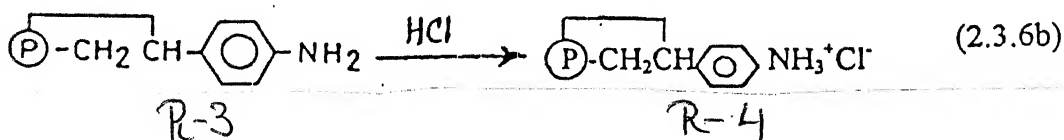
2.3.3. Amination of Nitrated PS-DVB Resin :

Amination of nitrated R-2 polystyrene-divinylbenzene resins is carried out with hydrazine hydrate. 1.5 g of surface nitrated PS-DVB resins are placed in a conical flask with 50 ml of hydrazine hydrate. The inside temperature of the reaction mass is maintained at 50°C for four hours in an oil bath maintained at about 60°C . After this time is over, the resin is filtered, and then properly washed with distilled

water and dried in an oven overnight. These aminated resin is ready for further processing. The capacity of R-3 resin can be determined through the procedure given in section 2.3.4 and its formation can be represented by



The R-3 resin on reaction with HCl is likely to give an exchangeable chloride ion as follows:



2.3.4 Determination of Capacity

2.3.4.1 Titration Method:

This method is based on the fact that all amine groups would react with HCl to give an ammonium salt as in eq. 2.3.6b. In view of this, the procedure consists of placing approximately 1.5 g of aminated resin in a conical flask and heating it with 50 ml of 0.1N HCl for four hours at 50 °C. The reaction mass is then filtered and the filtrate contained unconsumed HCl which is titrated with 0.1N NaOH to determine the chlorine ion intake by the aminated R-3 resin. The titration is carried out using phenolphthalein indicator (1% solution in ethanol). Again the carefully washed and dried aminated R-3 resin is heated with 0.1N NaOH for four hours at 50 °C. The concentration of the remainder NaOH is determined by titration with 0.1N HCl using phenolphthalein indicator. The capacity of aminated resin is calculated by the following relation.

$$N_{NaOH} = \frac{V_{HCl}}{V_{NaOH}} N_{HCl} \quad (2.3.7)$$

$$\text{The capacity of resins in meq/g} = \frac{50(0.1 - N_{NaOH})}{1000} \quad (2.3.8)$$

2.3.4.2 Gravimetric Method:

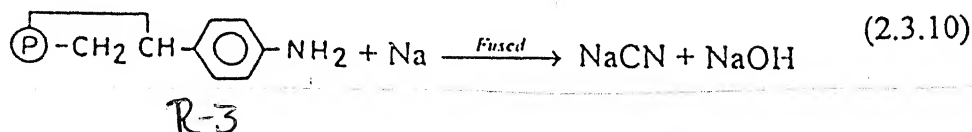
Alternatively the exchange capacity of the aminated R-3 resin can be determined using the method given in ASTM standard No. ASTM D (2187, 2687, 3087, 3375 and ISI).¹¹⁰ In the recommended procedure mixed acid is first prepared by mixing 18.1 ml of H₂SO₄ (sp.gr.1.84) with 27.5 ml of HCl (sp.gr.1.19) in 500 ml of distilled water. The entire content is made up to 1000 ml using distilled water. After this, the test water is prepared by diluting the mixed acid with distilled water upto 1% concentration. This test water is then added to the aminated R-3 resin in a quantity of 100 ml per gram and kept for 24 hrs. After this the resin is filtered and washed with distilled water till the filtrate become neutral which is concluded by observing whether the colour of methyl orange changes from orange red to orange yellow. This way we get resin which is free from the mixed acid. This resin is then mixed with 0.1N NaNO₃ solution (8.5 g in 1000ml distilled water) and kept for another 24 hrs. Then the reaction mass is filtered and the filtrate is added to 1.7 g of AgNO₃ with 2-3 drops of HNO₃ and the entire mass is kept for 24 hrs. The chlorine ion present in the filtrate form AgCl which is a precipitate of AgCl. This precipitate is filtered, dried and weighed and the capacity of aminated R-3 resin is calculated by using the following relation.

$$\text{Capacity (meq/g)} = \frac{\text{Weight of the Precipitate}}{\text{Molecular Weight of AgCl}} \quad (2.3.9)$$

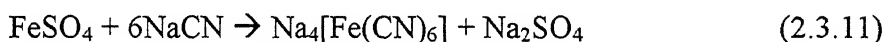
The capacity obtained by this gravimetric estimation method is then compared with the titration method described earlier.

2.3.5 Elemental Test for Nitrogen Detection in PS-DVB Resin

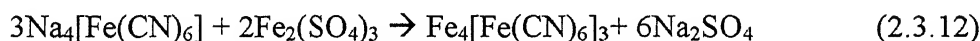
In order to detect nitrogen in the R-3 PS-DVB resins, the Lassaigne element spot detection test has been slightly modified. In this element nitrogen detection test, the polymer resin is fused with metallic sodium to form sodium cyanide as follows:



After the fusion reaction is over, the entire content is washed with water and 2-3 ml of this filtrate solution is poured into a test tube containing 0.1-0.2 g of powdered iron (II) sulphate crystals.



The mixture is then heated gently with shaking, then without cooling, dilute sulfuric acid is added to dissolve the metallic hydroxides and a prussian blue colour of the mixture formed confirms the presence of nitrogen.



2.3.6 Measurement of Internal Surface Area of PS-DVB Resin:

Measurement of internal surface area of polymer resins is made using standard BET isotherm apparatus (Pulse Chemisorb 2700). This instrument works on a simple principle of BET adsorption isotherm. The surface area of the resins is determined by following relation:

$$S = V_m A (N/M) \quad (2.3.13)$$

In this reaction V_m is the volume of gas (STP) required to form an adsorbed monomolecular layer, A is the Avogadro's number which expresses the number of gas molecules in a mole at standard conditions, M is the molar volume of the gas and N is the area of each adsorbed gas molecule.

Measurement of surface area is done by passing the carrier gas in the ratio of 30% N_2 and 70% He through the sample. The nitrogen is used as an adsorbate gas and helium is the carrier gas. The sample holder is immersed in the liquid nitrogen bath at a very low temperature (-197°C). Adsorption of nitrogen over the surface of sample gives the surface area of the sample.

2.3.7 Bond Energy Determination through Electron Spectroscopy for Chemical Analysis (ESCA)

In this technique, surfaces are bombarded with particles of high energy like electrons, photons, and ions. Quantitative/qualitative elemental information can be deduced from the ESCA by determining the specific bond energies for elements. Incident photons are generated from aluminium K_α and are bombarded on solid surface of polystyrene-divinylbenzene copolymer resins. This generates inner shell electrons known as photo-electrons and their kinetic energy distribution from which the binding energies are calculated. This technique is a one level transition process and gives chemical states of elements on the surface by measuring the chemical shifts in addition to the elemental detection capability.

The instrument used in this study ESCA VG MK.II by VG Scientific, UK. For determining the binding energy of different elements presents in the surfaces of PS-DVB resins, the sample is first baked for 8-10 hrs at $170-200^\circ\text{C}$. This operation is performed for obtaining the clean surface and is necessary whenever vacuum is broken or the sample is changed. After proper baking, the sample is introduced to

sample holding track/tray in the main chamber by sample transport mechanism. Our sample is in the form of 1mm size resin resins and the vacuum inside the system is maintained 10^{-9} mm Hg survey scan is taken in the two regions of 0-500 eV and 500-1000 eV respectively. As per the survey scan and depending upon the nature of modifications carried out, various peaks of different elements are obtained. After this information and the information available from standard samples, each element is individually scanned for different binding energy range. In our case the elements scanned are Carbon, Nitrogen and Oxygen. This gives rise to their respective peaks along with their binding energy regions in the survey scan. Thereafter, in order to analyze the binding energy of particular element and its shifting from its standard value, sample depth scan is taken individually for Carbon in the range of 275-325 eV, for Oxygen in the range of 525-575 eV and for Nitrogen in the range of 400-450 eV. The entire analysis is carried out for blank, nitrated and aminated resins of polystyrene-divinylbenzene copolymer. After getting the depth scan, peaks shifting from standard elements is calculated and thereby analyse the bond energy to distinguish the exact bonding and bond position of various functional groups (NO_2 and NH_2 in this case) positioned in PS-DVB resin.

2.4 Results and Discussion

The study of this chapter is divided into four sections and consists of (a) the formation of resins by suspension polymerization, (b) chemical characterization of the nitrate and amine functional groups on the surface (c) the reproducibility of experimental data on NO_x conversion and exchange capacity Q and (d) the time and temperature effects on nitration. These are individually discussed below.

2.4.1 Suspension Polymerization Of Crosslinked Macroporous Resin: In this study, crosslinked macroporous PS-DVB copolymer resin in the form of resins are prepared as per the recipe in sec.2.3.1. These polymeric resin are macroporous in nature because of the use of toluene as a diluent in the organic phase which is a good solvent for linear polystyrene chains. The PS-DVB resin has been characterized for their particle size distribution and internal surface area by varying the amount of different ingredients, the nature and fraction of diluent and the amount of gelatin of the recipe. In this work we have changed the nature of the diluent by mixing n-heptane (which is a non solvent to linear polystyrene) with toluene as the solvating medium. To determine the effect of this ratio on the internal surface area and particle size distribution of the resin formed, the internal surface area measurements have been made using the procedure given in sec 2.3.6 and results are summarized in Table 2.1. It is observed that the suspension polymerization technique of forming polymer resins cannot be used beyond 40% heptane because the organic material and water separate out and the polymer forms in one big lump. However for heptane less than this, as the percentage of heptane is increased, the internal surface area is found to reduce. In the presence of a solvating diluent toluene, the formed resin are in the swollen state and its degree of swelling reduces by the presence of a nonsolvent. In the case of a nonsolvent diluent, the polymer chains are more entangled and thus form a compact structure with lower internal surface area. The particle size distribution are measured by sieving and result have been plotted in Figure2.3. This Figure shows that the particle size distribution is extremely sharp and its shape is found not to be affected by the percent ratio of the nonsolvent n-heptane present. The average particle size goes down as the amount of n-heptane increases and the reason for this is not quite clear.

In the next phase of the study, only toluene is used as the solvating medium and the effect of gelatin content in the aqueous phase has been examined. It is found that this plays a major role on the particle size distribution as well as the internal surface area of the resin. The experiments are conducted using different gelatin contents in each run and the results are shown in Figure 2.4 . The particle size distribution obtained for each run is found to be extremely sharp. It is found that increasing gelatin content reduces the average size of resins as shown in the Figure 2.5. It is found through the experimental results that there is a critical gelatin concentration, C_{crit} , below which resins are unstable and form an agglomerate to give a large polymer mass.

Internal surface area of the resin formed is another property which is influenced by the amount of gelatin content in water. It is found that the internal surface area increases with the increase in gelatin content which is shown in Figure 2.6 . From Figures. 2.5 and 2.6 it is seen that there is an optimal value of gelatin content for which the average size of particle and internal surface area, both give optimal performance. In this study the value of gelatin content is chosen as 0.028g/100 ml of water which gives average particle size of 1mm and internal surface area of $9.33 \text{ m}^2/\text{g}$.

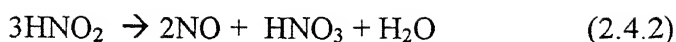
2.4.2 Nitration of Polystyrene-Divinylbenzene Resins:

Using the procedure given in section 2.3.1, the PS-DVB copolymer resin has been prepared so that their average particles are large and have size lying between (1mm to 1.5mm) by keeping the amount of gelatin as 0.028 g in the recipe. Resins of uniform size are separated by sieving and these are subjected to nitration. We first carried out the nitration of polymer resin using NO_x in a small glass bottle with 1.2

mm opening at the mouth sealed with injectable silicone rubber septum. About 0.5 g of PS-DVB resins are placed inside the bottle and NO_x is injected in it using a 25 ml syringe. The bottle is placed inside an oven to carry out the reaction and after 3-4 hrs the bottle is withdrawn. It is found that the surface nitration reaction occurred sufficiently. In order to accommodate large amount of gas, we chose to work with relatively larger glass reactor (2.5 litre) to accommodate the NO_x without increasing the reactor pressure significantly at the reaction temperature. The length of the reactor is 30cm and diameter 10.5 cm with a 2.54cm opening at its mouth. The mouth of this bottle is closed with an aluminium cap having threads inside because aluminium is found to be practically unaffected by NO_x and is relatively inexpensive. This cap is supported by Teflon seals inside having a 1.2 mm opening at its upper portion. A 10 mm silicone rubber septum is fitted inside the opening through which a needle is punctured to create a slight vacuum inside. The Silicone rubber septum can withstand a temperature of upto 300°C and facilitates introduction of gas mixture of known amount and ratio of oxygen and NO_x . To carry out the reaction smoothly a large oven was procured which could accommodate atleast six reaction vessels at a given time.

The effect of different reaction parameters upon the extent of surface nitration has been examined by varying the temperature, the amount of the gas fed and the time of reaction. For each set of reaction, the amount of consumed NO_x has been determined by injecting 100 ml of distilled water to the reactor to dissolved the remaining NO_x followed by vigorous shaking. This converts the residual gas within the reaction into nitric acid (HNO_3) according to¹¹²

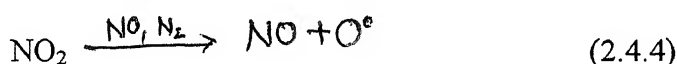




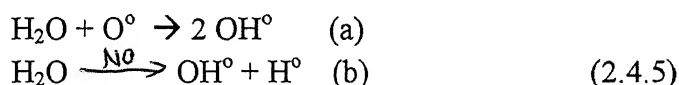
After this the polymer R-2 resin is separated and the filtrate comprises HNO_3 solution which is pale yellow in colour. This solution is titrated with 0.1N NaOH to determine the strength of HNO_3 in water and the consumed NO_x is determined with the knowledge of the initial amount of NO_x introduced into the reaction bottle.

There are few problems associated with evaluation of consumed NO_x . It is very difficult to dissolve all the NO_x completely. This is likely to affect the results, however we have endeavoured to minimize this loss. After this the polymer resins are washed, dried and kept in a desiccator. The nitrated R-2 resin is found to have a colour change from white to golden yellow as shown in the Figure 2.7.

The reactions involving NO_x have been well studied in problems of pollution phenomena arising due to NO_x in atmosphere^{115,116}. The reactions are assumed to be triggered by nitrogen and the NO_2 produce O radical as follows



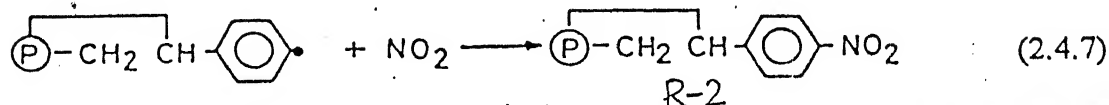
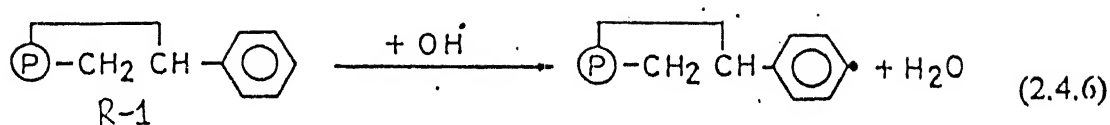
and these oxygen radicals react with moisture to give OH^\bullet radical as follows



These hydroxyl radicals are active species which are assumed to give reactions involving NO_x . In more recent study¹¹⁷, the kinetics of formation of hydroxyl radical has been studied in the decomposition of peroxyxynitrons acid and the first order rate constants evaluated.

In our case, within the reactor, there is always air and moisture present in NO_x and reaction 2.4.1 and 2.4.2 can always occur giving hydroxyl radicals within it. Later on during the course of reaction water is generated as shown in equation 2.4.5.

These radicals can abstract hydrogen from the resin which can combine with NO_2 as shown below.



2.4.3 The FTIR Analysis Of the Resin

FTIR spectroscopy is one of the most useful technique for identification of functional groups. Functional groups present on the surface of the PS-DVB resin after the reaction are determined instrumentally by FTIR (Perkin Elmer 1600). The PS-DVB resins are first ground into fine powder and mixed with Potassium Bromide. The pellets of 1 cm size are prepared with the help of a hydraulic press and samples of blank, nitrated and aminated PS-DVB R-1, R-2 and R-3 resin have been used to determine FTIR spectra shown in the Figure2.8. There are a characteristic sharp peak of NO_2 present at $700, 1400 \text{ cm}^{-1}$ of nitrated PS-DVB resin. This confirms the presence of NO_2 group on the surface of PS-DVB resin. In the aminated sample R-3 of PS-DVB resin, there is a strong absorption near $3100 \text{ to } 3200 \text{ cm}^{-1}$ which confirms the presence of NH_2 group on the surface of PS-DVB resins with simultaneous disappearance of peak at 1400 cm^{-1} belonging to NO_2 .

2.4.4 Elemental Analysis through ESCA:

For determining the binding energy of different elements presents in the surface of PS-DVB resin, we carried out an ESCA analysis as described in Sec 2.3.7.

First we examined the samples of the blank, nitrated and aminated PS-DVB resins for survey scan in the range of 0-500 eV and 500-1000 eV. From this scan, each individual elements (Oxygen O 1s, Nitrogen N 1s and Carbon C 1s is scanned in its binding energy zone. After doing this, we prepared a scan in the range of 275-325 eV for carbon for those samples. A distinct peak of C 1s for carbon is observed at 284.2 eV in blank PS-DVB sample as expected. Thereafter the nitrated R-2 PS-DVB resin is scanned and a peak at 285.3 eV for C 1s is observed. There is a shifting of 1.1eV which confirms the change in carbon binding. Again in the aminated R-3 PS-DVB there is slight shifting in carbon C 1s peak position as shown in Figure 2.9(a). We then scanned Nitrogen N 1s in the range of 400-450 eV for all these three samples. A characteristic peak of nitrogen at 407 eV is present in the nitrogen range of 395-410 eV as shown in the Figure 2.9(b). The scan of the PS-DVB resins show the nitrogen N 1s peak at 405 eV showing a decrease in N 1s binding energy is aminated PS-DVB resins. This confirms the presence of bond between carbon and nitrogen and the NO_2 group is attached to phenyl ring.

2.4.5 Determination of NO_x Consumed during the reaction:

The unreacted NO_x was determined by dissolving it in distilled water. With vigorous shaking. The reaction takes place inside the reactor as described in equations 2.4.1, 2.4.2 and 2.4.3. The HNO_3 , which is pale yellow in colour is titrated with 0.1N NaOH to determine the strength of HNO_3 and this way the amount of consumed NO_x is determined. In this study we have examined the NO_x consumption during the nitration reaction with time as well as temperature and results are shown in Table 2.2 and are plotted in Figure 2.10. It is observed that on increasing the time and temperature, the NO_x consumption first increases and then attains an asymptotic

value for each temperature. At lower temperature, the NO_x reacted to the PS-DVB resin in lesser amount. However as we increase the temperature the reaction rate increases and at 130°C the reaction of NO_x to the surface is maximum. A substantial increase in NO_x consumption is observed between $100\text{--}110^\circ\text{C}$. We have already observed that at 140°C , the resin is shown to degrade and the fall in the NO_x consumption is because of polymer degradation occurring which changes the exchange characteristics.

2.4.6 Effect of Temperature on Nitration of PS-DVB Resin :

It is expected that the extent of nitration reaction would increase with increasing temperature. Therefore, the effect of nitration on PS-DVB resin is examined by varying the temperature at a step change of 10°C starting from 60°C upto 140°C . Beyond 140°C , the PS-DVB resins starts becoming brown in colour and therefore we did not examine temperatures more than this. The reaction time is set for nine hours, the NO_x consumption is determined every hour for entire set of experiment and results are shown in Figure 2.11. It is observed that the maximum consumption of NO_x took place at 130°C . Between 100 to 110°C the consumption jumps and thereafter it increases gradually upto 130°C . The R-2 resin is then aminated to R-3 using hydrazine hydrate, thereafter, the exchange capacity of this R aminated R-3 resin is determined and the results are shown in Figure 2.12. It is observed that the colour of the resin is changed from white to pale yellow as we increase the temperature from 60°C to 130°C and beyond this it become slightly darker to the naked eye and the colour remained the same as the temperature increases. The capacity results show that the maximum capacity is achieved at 130°C .

Since the capacity of the R-3 resin after amination reflects the extent of nitration, the nitration reaction could also be followed by titration and gravimetric

estimation techniques for R-3 resin as discussed in Sec.2.3.4. We observed that with the reaction time, the extent of nitration first increases rapidly but reaches an asymptotic value. It is found that most appropriate temperature to carry out the surface nitration of PS-DVB resin is 130° C beyond this temperature, there is no significant increase in nitration. Below 100° C very small nitration is achieved.

2.4.7 Reproducibility of Experimental Data:

In order to demonstrate the reproducibility of the experimental, we carried out the gas phase nitration of PS-DVB resin at 130 °C two more times. The results are summarized in Table 2.5. The resultant nitrated R-2 resin was aminated to form R-3 and its exchange capacity was determined gravimetrically. Since these nominated R-3 resin can not be regenerated, some of this resin was saved for further modification. As outlined in Chapter 3, these were first reacted with dichloroethane to give R-7 and then quarternized with the trimethylamine to give R-8. The final anion exchange resin is the same as run 8 and 9 of Table 3.2 and these were subjected to determination of exchange capacity and regeneration cycle for at least nine times. The results are once again summarized in Table 2.5.

The examination of Table 2.15 reveals that in the repeated experimentation, the amount of NO_x consumed is reproducible within 40% and that in the determination of exchange capacity, Q is within 6%. As oppose to this, in the regeneration cycle Q is reproducible within 5%.

2.4.8 Effect of Time of Nitration of Resin:

To study the effect of time on the nitration of PS-DVB resin, reaction was carried out for nine hours and samples were taken out on hourly basis. For this purpose, nine reactor bottles were put in the oven maintained at the desired

temperature. One reactor bottle was withdrawn on every hour, the reacted NO_x within the bottle is determined and the results plotted in Figure 2.10. The resin is then aminated and its capacity determined by both titration as well as gravimetrically and it is observed that on increasing the reaction time the nitration of PS-DVB resin increases and reaches an asymptotic value after 7-8 hours. On increasing the time of reaction the colour of the PS-DVB resin changes gradually from white to pale yellow and brown to naked eye. We have taken the photograph of this colour change and these are shown in Figure 2.13. Now to examine the formation of nitrate groups in R-1 resin, R-2 resin are converted to NH_2 groups and the capacity of the R-3 resin is determined. The experimental results are given in the Table 2.3 and 2.4 and the capacity results are plotted in Figure 2.14 upto 100°C and Figure 2.15 for temperatures beyond. It is observed that on increasing the reaction time the rate of nitration increases thus the capacity of the modified R-3 resin also increases and after 6-8 hrs of reaction it reaches an asymptotic value. It is also noticed that after 100°C the capacity increases significantly and a prominent jump in capacity is clearly visible in these figures.

It is recalled that 300 ml of NO_x or 13.39 mmoles of NO_x were completely consumed in the nitration reaction. If it is assumed that there is only one NH_2 group on the phenyl ring of R-3 resin, the anion exchanging group in R-4 resin would be NH_3^+Cl^- . In R-4 the molecular weight of the repeat unit $[-\text{CH}_2\text{CH}-\text{C}_6\text{H}_4\text{N}^+\text{H}_3\text{Cl}^-]$ would be 155.5 and would provide one exchangeable chloride ion. Let us assume N_0 is the number of repeat units of polymer chain. Since the resin R-4 is a network, ideally N_0 should be infinity, however for real chain let us assume this to be some large number. For this ensemble of chains, its molecular weight is $155.5 N_0$ and it gives N_0 chloride groups for exchange. In other words, on dry basis, it should give

a capacity of $N_o/(155.5 N_o)$ or 6.39 meq/g, a value which is independent of chain length. We have already observed 13.39 mmols of NO_x is completely reacted to each gram of the resin and in Table 2.5 we have observed the maximum capacity reached is 4.8 meq/g of wet resin. In Chapter 3, we have shown that the equilibrium moisture content of resin is 68% which means than on dry basis, the capacity would be $4.8/0.32$ or 15 meq/g of dry resin, which completes the material balance. In addition, this also suggest that a capacity of 15 meq/dry gram of resin can be explained only by multiple nitration of a given repeat unit. Secondly the resin reported in this work has low surface area with less than one percent of phenyl rings on the surface of internal pores. This suggest that most of the modification reaction must have occurred within the polymer gel phase with negligible reaction on the surface.

2.4.9 Determination of Rate Constant:

In the process of modification of polystyrene divinylbenzene copolymer resins, we carried out their gas phase nitration as the first step, followed by their amination. We have already discussed the chemistry of reaction in Section 2.4.2 and using NO_x conversion data we desire to determine the kinetics of the nitration reaction. Experimental results show that the NO_x intake during the nitration reaction increases asymptotically as the time of nitration increases.

In the previous section, we have shown that the nitration of polymer chains in R-2 resin is occurring within the gel medium. This means that according to basic mechanisms given in eqns.2.4.4 to 2.4.7, the hydroxyl radicals must be generated in the gas phase and then diffuse into the polymer gel along with molecules of NO_x . This suggests that the overall nitration reaction in 2.3.5 is a multiple step process and its mathematical analysis would be complex. In Appendix A2.1, we have assumed 1st, 2nd and 3rd order kinetics for the gas phase consumption of $[NO_x]$ versus t, data as

well as capacity Q , versus t data and carried out a linear regressional analysis using $y_{i,model} = ax_i + b$ type equation. Since at $t=0$, conversion of NO_x as well as Q is strictly zero, b in this relation is identically equal to zero. We have computed

$$S_r = \sum_{i=1}^n (y_i - y_{i,model})$$

$$S_t = \sum_{i=1}^n (y_i - \bar{y})$$

$$\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i$$

and $S_t > S_r$ implied that there is clustering of data and $y =$ is a better representation of data compared to a line passing through origin. The regressional analysis shows that in the 1st order kinetic model there is clustering and by increasing to the 2nd and 3rd order kinetic model the fit of the data improves considerably as seen from the values of coefficient of correlation r . We find the verse trend, when we start fitting the capacity Q versus t data. On increasing the order of the kinetic model, the coefficient of correlation r falls. Since we have already found that all NO_x molecules show up as nitrate groups in R-2 resin, it is expected that the kinetic order of both conversion of NO_x versus t and Q versus t should have the same order. This means that the regression analysis suggest the second order kinetic model.

2.4.10 Effect of Modification on Morphology:

It is desired to find out changes in the morphology of the surfaces due to modification reactions for which we developed SEM photographs at 1500 magnifications. These are shown in Figure 2.20 for unmodified resin, after modification with NO_x in R-2 and aminated R-3 resin after 5 hr of nitration. At lower magnification it does not show any substantial change over the surface of PS-DVB resin. From these figures, it appears that NO_x modification produces a

significant morphological change in R-2 resin over its surface. However amination reaction does not produce any substantial change as compared to nitrated surface of R-2. 54

2.4.11 Effect of Modification on Surface Area:

As discussed earlier, we determined the internal surface area of polymer particles as per the procedure described in section 2.3.6. We have already determined the surface area of unmodified resin, earlier and now we report the effect on this on NO_x modification and aminated resins over the time of reactions. The results are shown in Table 2.6 and we see no specific trend in these data. This is because on modification of the surface, its ability to retain moisture is considerably improved. We will be showing in Chapters 3 and 5 that the moisture is held with greater solvation energy and is difficult to remove. For determination of surface area, moisture content of the sample may block pores and may give misleading results. It is desirable that the sample should contain no moisture and should be completely dry for correct reading. In our case, we cannot remove moisture completely because of higher solvation energy of the resin after modification and most likely because of this reason, the information on surface area in Table 2.6 could not be trusted.

2.5 Conclusions:

In this chapter, we have developed a clean technology for nitration of PS-DVB resin because the entire NO_x is consumed during the reaction. Since the nitration reaction is irreversible in nature it is possible to carryout the gas-solid reaction in a closed vessel in which the NO_x is completely consumed. The consumption of NO_x could be determined by dissolving unreacted gas in water and the second order rate constant was this way determined. Total moles of NO_x reacted show that on a given repeat unit there are more than one point, on an average, where NO_2 reacted and most

of the reaction in gel region rather than limiting itself only on surfaces. The nitrated resin were subsequently aminated to R-3 resin and its exchange capacity determined using the usual ASTM procedure.

We have clearly demonstrated the bonded nitrogen in the resin and confirmed through FTIR, ESCA and the Lassaigne's spot test technique this way showing nitrate group formation within it. The SEM analysis of the modified resin clearly shows morphological change on the surfaces, while the surface area results showed poor reproducibility. This could possibly occur because chemical modifications make the resin more hydrophilic and the moisture retained inside cannot be removed by simple drying technique.

Appendix A2.1

Linear Regression Analysis Of Experimental data of NO_x consumption of Table 2.2 and data on Exchange Capacity of Resin of Table 2

Based on the Least Square regression of reference [17] we have determined

- 1) Sum of Square of residuals

$$Sr = \sum_{i=1}^n (y_i - a_0 - a_1 x_i)^2$$

r represents the error in the spread of data around the straight line $y_i = a_0 + a_1 x_i$.

- 2) Slope a_1 of the line $y_i = a_0 + a_1 x_i$

$$a_1 = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2}$$

- 3) Error in the spread of data around mean \bar{y}

$$St = \sum (y_i - \bar{y})^2$$

- 4) Standard Error of Estimate

$$S_{y/x} = \sqrt{\frac{Sr}{n-2}}$$

- 5) Correlation Coefficient, r

$$r = \frac{n \sum x_i y_i - (\sum x_i)(\sum y_i)}{\sqrt{n \sum y_i^2 - (\sum y_i)^2} \sqrt{n \sum x_i^2 - (\sum x_i)^2}}$$

$$= \left(\frac{S_t - S_r}{S_t} \right)^{1/2}$$

For a perfect fit $S_r=0$ and $r=1$ signifying that the line explains 100% of the variability of the data. For $S_t = S_r$ the fit represents no improvement.

For the data of conversion of NO_x versus time, we desire to determine the order n of the reaction in the following.

$$\frac{dC_A}{dt} = k C_A^n$$

We now examine the 1st, 2nd and 3rd order kinetics (or $n=1, 2$ and 3) and integrate the above equation to obtain the following

(1) Gas Model 1 ($n=1$)

$$-\ln(1-X_A) = k_1 t$$

(2) Gas Model 2 (for $n=2$)

$$\frac{X_A}{1-X_A} = k_2 C_{A0} t$$

(3) Gas Model 3 (for $n=3$)

$$\frac{2X_A - X_A^2}{(1-X_A)^2} = 2k_3 C_{A0}^2 t$$

Above X_A is the conversion of NO_x which is strictly zero at $t=0$. This implies that in the regression line $a_0=0$ and the number of data points in Table 2.2 is ten.

The analysis of experimental data of NO_x conversion versus t has been summarized in Tables A2.1 to A2.3. Theoretically $S_t > S_r$, whereas except for $T=463^\circ\text{K}$ in Table A2.1, in every case $S_r > S_t$, a result which was of great surprise to us. It clearly indicates distribution of data around mean gives less total error S_t thus representing the data on $y = \bar{y}$ gives less total error. After checking the computer result, with long hand calculations and ascertaining the correctness of the computed results, we conclude that the assumption of 1st order kinetics is a poor one. The assumption of 2nd order kinetics in Table 2 shows that for 4 out of nine

temperatures studied, $S_r > S_t$. As opposed to this for $n=3$, such condition does not arise and correlation coefficient for the data is above 60%.

For solid phase kinetic studies for exchange capacity, Q versus t data of Table 2.5, We assume that every molecule of NO_x reacted shows up as an NH_2 groups within the resin. In view of this, the integrated 1st, 2nd and 3rd kinetic model can be written by replacing X_{NO_x} with Q/Q_∞ to obtain

(1) Solid Model 1

$$-\ln \left(1 - \frac{Q}{Q_\infty} \right) = k_1 t$$

(2) Solid Model 2

$$\frac{Q/Q_\infty}{1 - Q/Q_\infty} = k_2 Q_\infty t$$

(3) Solid Model 3

$$\frac{\left(\frac{Q}{Q_\infty} \right) (2 - Q/Q_\infty)}{(1 - Q/Q_\infty)^2} = 2k_3 Q_\infty^2 t$$

Above Q_∞ is the asymptotic exchange capacity (at $t = \infty$).

The experimental data on exchange capacity Q of Table 2.5 have been analysed and results presented in Table A2.4 to A2.6 for different kinetic models. A careful examination of these tables reveal that in these $S_t > S_r$ which implies that it is possible to determine best line passing through origin. In Table A2.4 for 1st order solid model 1, except for $T=120^\circ\text{C}$, the correlation coefficient r was above 75%. As the kinetic order n is increases, results of Tables A2.5 and A2.6 show that the fit becomes poorer.

Table 2.1**Effect of Nature of Diluent on the Internal Surface Area**

Percentage Heptane	Internal Surface Area (m²/g)
0	9.88
10	6.33
20	5.03
30	3.86
40	Organic and Water layer demix and polymer formed in one lump

Table 2.2

Volume of NO_x Consumed (in ml/1.5 g) During the Surface Nitration Reaction

Time/Temp (hr)	Volume of NO _x consumed in ml				
	60 °C	70 °C	80 °C	90°C	100°C
0.5	201.89	173.00	193.01	208.91	206.99
1.0	190.31	191.01	202.33	201.36	206.44
1.5	171.22	191.00	181.39	210.36	219.79
2.0	191.62	195.03	197.33	217.64	215.66
3.0	200.01	197.73	230.01	213.39	261.76
4.0	206.00	201.59	217.66	218.59	232.91
5.0	207.42	210.71	214.11	231.92	249.77
6.0	209.66	215.69	217.37	230.33	251.36
7.0	211.73	213.11	216.91	235.74	251.77
8.0	291.67	212.12	243.11	234.39	259.66
9.0	208.11	213.66	214.02	265.00	254.00

Table 2.2

Volume of NO_x Consumed (in ml/1.5g) during the Surface Nitration Reaction

Time/Temp (hr)	Volume of NO _x consumed in ml			
	110 °C	120 °C	130 °C	140°C
0.5	201.39	235.36	216.11	221.36
1.0	206.44	215.27	226.35	236.41
1.5	219.79	226.29	229.91	231.61
2.0	225.66	249.31	235.61	240.37
3.0	241.98	268.73	255.38	246.11
4.0	265.39	281.59	281.57	271.66
5.0	279.77	295.36	309.57	310.36
6.0	281.36	289.17	311.63	306.65
7.0	284.47	294.81	306.11	301.65
8.0	289.00	281.93	310/41	309.96
9.0	284.92	293.00	315.91	301.37

Table

Capacity (mmloes/g)

Time/Temp	110	120	130	140
0.5	0.391	0.461	0.837	0.991
1.0	0.472	0.596	0.911	0.956
1.5	0.673	0.832	0.871	0.727
2.0	0.731	0.947	0.991	1.000
3.0	0.217	1.000	1.217	1.231
4.0	0.841	1.139	1.419	1.476
5.0	0.839	1.247	1.548	1.592
6.0	0.836	1.213	1.511	1.641
7.0	0.849	1.213	1.511	1.592
8.0	0.845	1.241	1.744	1.636
9.0	0.844	1.249	1.749	1.421

Table 2.3

Measurement of Exchange Capacity (in meq/g) of PS-DVB Resin by Gravimetric Estimation

Duration Of Reaction (hr)	60°C			70°C			80°C		
	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)
1	0.7259	0.0023	0.040	0.8706	0.0054	0.043	0.4835	0.0062	0.089
2	0.3936	0.0023	0.040	0.9899	0.0129	0.091	0.5140	0.0379	0.196
3	0.2972	0.0022	0.051	0.4967	0.0034	0.048	0.4300	0.0122	0.199
4	0.9576	0.0073	0.053	0.6429	0.0057	0.061	0.6999	0.0237	0.236
5	0.7885	0.0068	0.060	0.6447	0.0055	0.059	0.5780	0.0203	0.254
6	0.6097	0.0054	0.062	0.5092	0.0045	0.061	0.4606	0.0163	0.247
7	0.8781	-	0.091	0.7856	0.1003	0.890	0.4941	0.0176	0.248
8	0.7634	0.0100	0.062	0.4888	0.0046	0.066	0.4928	0.0174	0.246
9	0.5224	0.0044	0.059	0.5858	0.0057	0.068	0.5437	0.0115	0.1407

Table 2.3

Measurement of Exchange Capacity (in meq/g) of PS-DVB Resin by Gravimetric Estimation

Duration Of Reaction (hr)	90°C			100°C			110°C		
	Wt. of Resin (g)	Wt. of ppt (g)	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)	Capacity (meq/g)	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)
1	0.3225	0.0031	0.5230	0.535	0.713	0.066	0.4599	0.0387	0.586
2	0.4151	0.0155	0.4597	0.0565	0.856	0.260	0.5043	0.0151	0.208
3	0.5396	0.0216	0.5594	0.0131	0.198	0.279	0.4817	0.0199	0.281
4	0.4218	0.0197	0.5408	0.0735	0.947	0.326	0.4771	0.0301	0.439
5	0.5047	0.0236	0.5298	0.0756	0.994	0.327	0.5590	0.0356	0.444
6	0.5732	0.0276	0.6469	0.0926	0.997	0.336	0.5183	0.0339	0.456
7	0.5401	0.0263	0.5578	0.0759	0.948	0.339	0.4710	0.0302	0.447
8	0.4975	0.0243	0.6012	0.0845	0.980	0.341	0.5504	0.0351	0.445
9	0.4521	0.0219	0.4216	0.0602	0.995	0.338	0.6506	0.0387	0.414

Table 2.3

Measurement of Exchange Capacity (in meq/g) of PS-DVB Resin by Gravimetric Estimation

Duration Of Reaction (hr)	120°C			130°C			140°C		
	Wt. of Resin (g)	Wt. of ppt (g)	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)	Capacity (meq/g)	Wt. of Resin (g)	Wt. of ppt (g)	Capacity (meq/g)
1	0.6066	0.0863	0.6121	0.0826	0.940	0.992	0.6315	0.8319	0.918
2	0.5818	0.0809	0.5890	0.0848	1.003	0.969	0.5400	0.0785	1.013
3	0.6070	0.0955	0.4943	0.0935	1.318	1.096	0.5930	0.1085	1.275
4	0.5699	0.1071	0.5256	0.1085	1.439	1.311	0.5542	0.1172	1.474
5	0.5781	0.1134	0.6299	0.1415	1.565	1.367	0.6292	0.1380	1.528
6	0.4999	0.1089	0.4967	0.1153	1.617	1.519	0.5695	0.1455	1.780
7	0.5785	0.1397	0.5509	0.1100	1.392	1.683	0.5305	0.1299	1.707
8	0.6254	0.1393	0.5490	0.1190	1.511	1.552	0.4598	0.0801	1.214
9	0.4340	0.0951	0.5317	0.0763	1.000	1.527	0.5273	0.1287	1.701

Table 2.4

Measurement of Exchange Capacity by Titration (in mmol/g) of PS-DVB Resin with duration of Reaction of NO_x as parameter

Duration Of Reaction (hr)	60°C			70°C			80°C		
	Wt. of Resin (g)	Titre Value(ml)	Wt. of Resin (g)	Titre Value(ml)	Capacity (mmol/g)	Capacity (mmol/g)	Wt. of Resin(g)	Titre Value(ml)	Capacity (mmol/g)
1	1.4885	49.9	1.4939	48.9	0.074	0.0201	1.4792	49.2	0.054
2	1.4790	49.2	1.5186	47.1	0.191	0.054	1.5147	48.7	0.086
3	1.4533	49.3	1.6005	46.9	0.194	0.048	1.5897	49.5	0.038
4	1.4698	49.2	1.4522	47.2	0.193	0.054	1.5341	49.2	0.052
5	1.5144	48.8	1.4847	46.7	0.223	0.079	1.4308	49.7	0.021
6	1.3426	49.3	1.4828	46.5	0.236	0.052	1.4314	49.5	0.035
7	1.4711	48.8	1.4987	46.4	0.240	0.082	1.4579	48.8	0.082
8	1.4557	49.1	1.5688	46.4	0.229	0.062	1.5122	49.0	0.066
9	1.4718	49.2	1.3807	46.6	0.246	0.054	1.4581	49.0	0.068

Measurement of Exchange Capacity by Titration (in mmol/g) of PS-DVB Resin with Duration of Reaction of NO_x as Parameter

Duration Of nitration (hr)	90°C			100°C			110°C		
	Wt. of Resin (g)	Titre Value(ml)	Wt. of Resin (g)	Titre Value(ml)	Capacity (meq/g)	Capacity (mmol/g)	Wt. of Resin (g)	Titre Value (ml)	Capacity (mmol/g)
1	1.4642	48.8	1.4173	43.3	0.472	0.082	1.4225	48.0	1.141
2	1.3664	47.3	1.4254	39.5	0.736	0.197	1.5971	46.9	0.194
3	1.4484	46.4	1.3904	46.9	0.223	0.247	1.4498	45.3	0.324
4	1.5162	45.5	1.5059	37.3	0.843	0.297	1.4374	45.1	0.340
5	1.6186	45.3	1.4543	37.7	0.845	0.290	1.5449	44.7	0.343
6	1.4573	45.7	1.5226	37.2	0.841	0.295	1.4714	45.0	0.339
7	1.4334	45.7	1.5247	37.0	0.852	0.294	1.5275	44.7	0.346
8	1.3796	45.9	1.4553	37.7	0.846	0.297	1.3521	45.4	0.340
9	1.6138	45.1	1.4409	37.8	0.846	0.303	1.5192	44.8	0.342

Measurement of Exchange Capacity by Titrator (in mmol/g) of PS-DVB Resin with duration of Reaction of NO_x as parameter

Duration (hr)	120°C			130°C			140°C		
	Wt. of Resin (g)	Titre Value (ml)	Capacity (meq/g)	Wt. of Resin (g)	Titre Value (ml)	Capacity (meq/g)	Wt. of Resin (g)	Titre Value (ml)	Capacity (mmol/g)
1	1.6086	40.4	0.596	1.5176	36.1	0.915	1.4478	36.1	0.960
2	1.4724	36.0	0.950	1.3745	36.3	0.996	1.4130	35.8	1.004
3	1.5243	34.7	1.003	1.3977	32.9	1.223	1.3858	32.9	1.234
4	1.5399	32.4	1.142	1.3952	30.2	1.419	1.4217	29.0	1.477
5	1.4579	31.8	1.248	1.4317	27.8	1.551	1.4633	26.7	1.592
6	1.4917	31.9	1.213	1.4251	28.4	1.515	1.4507	27.6	1.544
7	1.3843	33.2	1.213	1.5123	27.1	1.514	1.5044	26.0	1.595
8	1.4655	31.8	1.241	1.5163	23.5	1.747	1.3767	30.1	1.445
9	1.4460	31.9	1.251	1.3957	25.5	1.755	1.3996	30.1	1.421

Table 2.5
Results on Reproducibility of Nitration of PS-DVB Resin at 130°C

Duration of Run.(hr)	Run 1			Run 2			Run 3		
	1	2	3	1	2	3	1	2	3
1	226.35	0.992	3.64	192.45	0.961	3.62	216.7	0.981	3.69
2	235.62	0.969	4.09	262.4	0.995	3.98	251.5	0.971	4.13
3	155.38	1.096	4.36	270.5	1.215	4.62	263.2	1.138	4.36
4	281.57	1.311	4.83	290.6	1.367	4.83	295.4	1.329	4.73
5	309.57	1.367	1.94	310.2	1.452	4.67	320.2	1.423	4.69
6	311.63	1.519	4.90	308.5	1.531	5.21	302.5	1.528	5.28
7	306.11	1.683	3.14	315.0	1.695	3.25	312.5	1.725	3.28
8	310.41	1.552	3.92	310.5	1.589	3.99	316.7	1.639	3.67
9	315.91	1.527	3.61	312.0	1.497	3.82	315.0	1.535	4.26
10	-	-	2.79	-	-	3.13	-	-	2.87
11	-	-	2.44	-	-	2.61	-	-	2.58
12	-	-	2.07	-	-	2.23	-	-	2.43

- 1 : ml of NO_x consumed at 130°C
 2 : exchange capacity of R-3 resin in meq/g of wet resin found at 130°C
 3 : Exchange capacity of R-8 Resin obtained by modification of R-3 Resin by Trimethylamine in meq/g of wet resin formed at 130°C

Table 2.5 (continued)

Reproducibility of Capacity of R-8 Resin formed from Run 1 after 6 and 12 hr of Nitration

Regeneration Cycle No.	1	2
1	5.31	2.00
2	4.49	2.14
3	5.25	2.21
4	5.38	2.06
5	4.89	2.16
6	5.09	2.11
7	4.99	2.38
8	5.21	2.17
9	5.22	2.14

- 1 Capacity of TMA modified R-8 resin formed in Run 1 after 6 hrs of nitration in meq/g of wet resin
- 2 Capacity of TMA modified R-8 resin formed in Run 1 after 12 hrs of nitration in meq/g of wet resin

Table 2.6

Change in Surface Area of PS-DVB Resin due to Modification

Type of Resin	Surface Area (m ² /gm)
Unmodified PS-DVB Resin	9.879
Surface Nitrated PS-DVB Resin	2.447
Aminated PS-DVB Resin (one hour)	2.539
Aminated PS-DVB Resin (Two hour)	2.840
Aminated PS-DVB Resin (Three hour)	2.861
Aminated PS-DVB Resin (Four hour)	3.377
Aminated PS-DVB Resin (Five hour)	3.594
Aminated PS-DVB Resin (Six hour)	4.135
Aminated PS-DVB Resin (Seven hour)	6.297
Aminated PS-DVB Resin (Eight hour)	5.031
Aminated PS-DVB Resin (Nine hour)	4.938
DOWEX	1.243

Table A2.1
Regression Analysis of 1st Order kinetics to [NO_x] versus t data in the
nitration of PS-DVB resin

T ^o K	k ₁ , hr ⁻¹	Sr	St	R	σ
333	0.185	2.608	2.171	Z	0.390
343	0.151	1.931	0.788	Z	0.338
353	0.157	2.166	0.910	Z	0.345
363	0.169	2.068	1.028	Z	0.338
373	0.177	2.365	1.169	Z	0.371
383	0.203	1.892	1.750	Z	0.343
393	0.206	2.597	1.684	Z	0.403
403	0.218	1.896	2.155	-0.346	0.351
413	0.200	1.963	1.708	Z	0.349

Z: Sr > St means that line $y = \bar{y}$ gives less total error compared to $y = ax$ line passing through origin $k_1 = 0.67 \exp\left(-\frac{478.82}{T}\right)$

Table A2.2
Regression Analysis of 2nd order kinetics to [NO_x] versus t data for Nitration of
PS-DVB resin

T °K	k ₂	Sr	St	r	σ
333	81.97	21.060	28.561	0.512	0.931
343	51.26	4.344	2.288	Z	0.514
353	54.44	5.398	3.049	Z	0.536
363	61.52	4.705	3.962	Z	0.499
373	66.08	6.172	4.596	Z	0.592
383	84.36	3.957	9.622	0.767	0.499
393	85.53	7.171	8.915	0.472	0.676
403	96.43	4.046	14.387	0.847	0.518
413	82.03	4.715	9.483	0.709	0.530

Z : Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_2 = 4.65 \times 10^2 \exp \left(-\frac{692.09}{T} \right)$$

Table A2.3
Regression Analysis of 3rd order kinetics to $[\text{NO}_x]$ versus t data for
Nitration of PS-DVB resin

T °K	k_2	Sr	St	r	σ
333	4.985×10^{-4}	2.025×10^{-4}	2.655×10^{-3}	0.487	7.686
343	1.855×10^{-4}	4.298×10^{-1}	3.193×10^{-1}	Z	1.642
353	2.043×10^{-4}	6.516×10^{-1}	5.271×10^{-1}	Z	1.914
363	2.471×10^{-4}	5.211×10^{-1}	8.613×10^{-1}	0.628	1.734
373	2.709×10^{-4}	8.001×10^{-1}	9.429×10^{-1}	0.389	2.014
383	3.995×10^{-4}	3.664×10^{-1}	2.832×10^{-1}	0.933	1.388
393	4.050×10^{-4}	1.061×10^{-2}	2.578×10^{-2}	0.767	2.576
403	4.990×10^{-4}	5.392×10^{-1}	5.253×10^{-2}	0.947	1.617
413	3.841×10^{-4}	7.064×10^{-1}	2.839×10^{-2}	0.866	1.766

Z : $\text{Sr} > \text{St}$ means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_1 = 2.899 \times 10^4 \exp\left(-\frac{813.65}{T}\right)$$

Table A2.4
Regression analysis of order kinetics to $[Q]$ versus t for the capacity of PS-DVB resin

T °C	k_{Q1}	S_r	S_t	R	Mean Dev.
60	0.444	2.963	8.584	0.809	0.495
70	0.435	0.749	7.678	0.949	0.245
80	0.525	1.242	14.981	0.957	0.295
90	0.628	14.121	39.949	0.804	1.003
100	0.636	2.200	28.839	0.961	0.385
110	0.460	7.744	17.394	0.744	0.752
120	0.313	8.936	9.029	0.101	0.751
130	0.321	0.856	5.823	0.923	0.232
140	0.331	3.583	9.191	0.781	0.453

Z : $S_r > S_t$ means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{Q1} = 0.061 \exp \left(-\frac{734.46}{T} \right)$$

Table A2.5
Regression Analysis of 2nd order kinetics to Q versus t data for capacity of PS-DVB resin.

T °C	k _{Q2}	Sr	St	r	σ
60	43.871	3.433 x 10 ²	7.675 x 10 ²	0.743	4.893
70	38.259	2.705 x 10 ²	7.581 x 10 ²	0.802	4.787
80	17.984	3.609 x 10 ²	2.047 x 10 ³	0.907	6.007
90	27.480	1.744 x 10 ⁵	2.645 x 10 ⁵	0.583	113.939
100	37.520	1.081 x 10 ⁴	2.899 x 10 ⁴	0.791	25.651
110	9.328	1.753 x 10 ³	2.826 x 10 ³	0.616	12.263
120	0.926	6.816 x 10 ²	7.304 x 10 ²	0.258	4.964
130	0.715	1.890 x 10 ¹	1.511 x 10 ²	0.930	1.256

Z : Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{Q2} = 9 \times 10^{-9} \exp \left(-\frac{766.00}{T} \right)$$

Table A2.6
Regression Analysis of 3rd order kinetics to Q versus t data for capacity of PS-DVB Resin.

T°C	k_{Q3}	Sr	St	R	σ
60	8.44×10^3	5.194×10^5	7.946×10^5	0.588	194.6
70	7.513×10^3	6.257×10^5	1.068×10^6	0.643	237.0
80	1.272×10^3	1.171×10^6	3.625×10^6	0.822	335.2
90	5.698×10^3	42×10^9	59.3×10^9	0.540	53251.7
100	6.864×10^3	47×10^7	78.03×10^7	0.629	5229.1
110	0.415×10^3	47.4×10^5	67.5×10^5	0.546	573.9
120	0.072×10^3	7.7×10^5	7.86×10^5	0.147	159.2
130	2.615×10^3	8.203×10^3	3.010×10^4	0.852	25.1
140	5.386×10^3	27.22×10^4	45×10^4	0.628	138.8

Z : $Sr > St$ means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{Q3} = 3.80 \times 10^{-4} \exp \left(- \frac{1.38 \times 10^4}{T} \right)$$

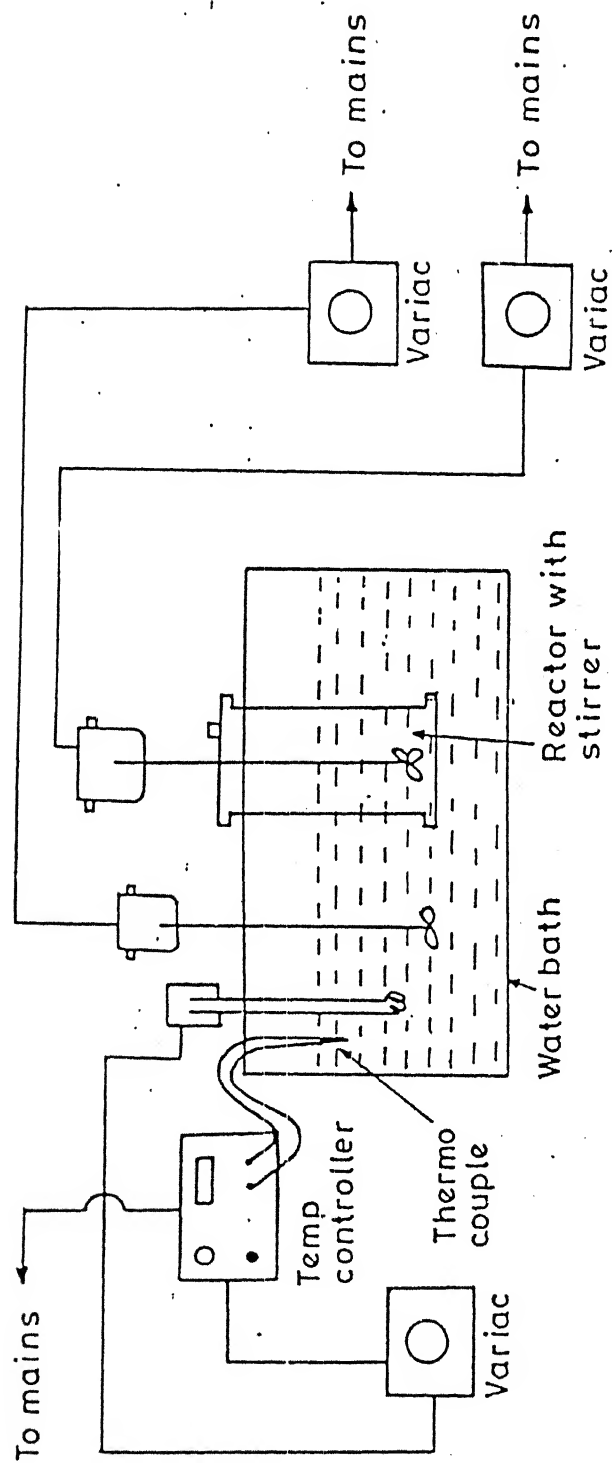


Figure 2.1 : Experimental Set up for the Preparation of PS-DVB Resin

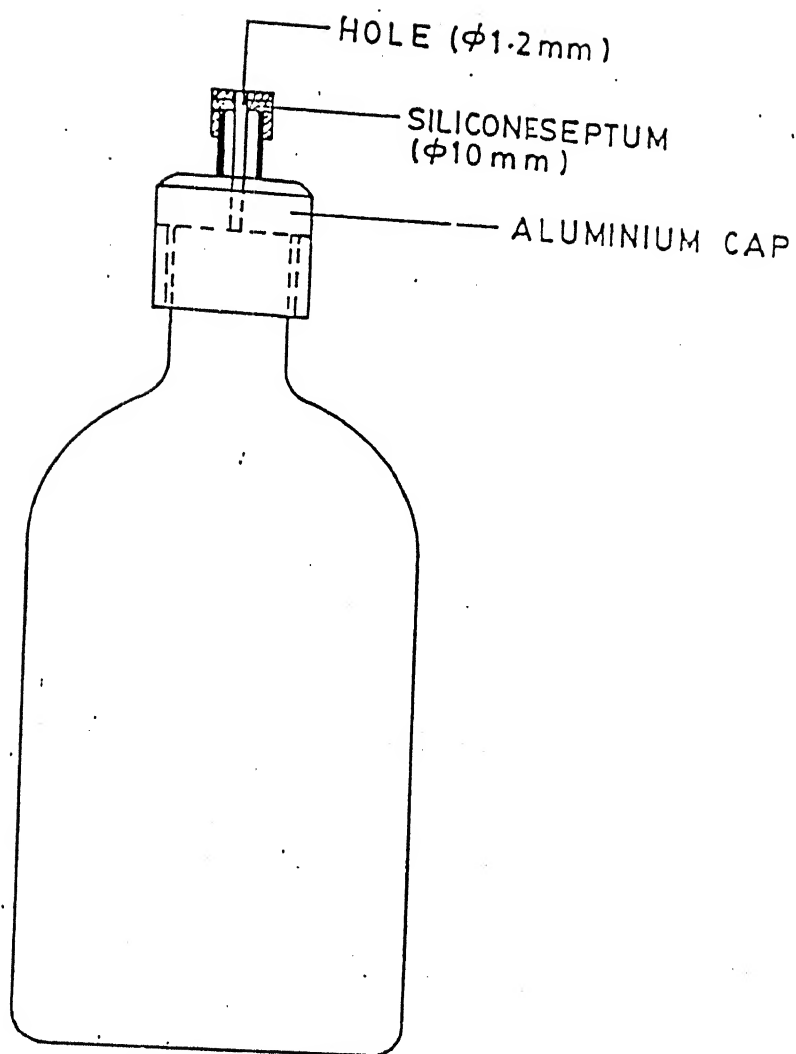


Figure 2.2 : Reactor used for Nitration of PS-DVB Resin

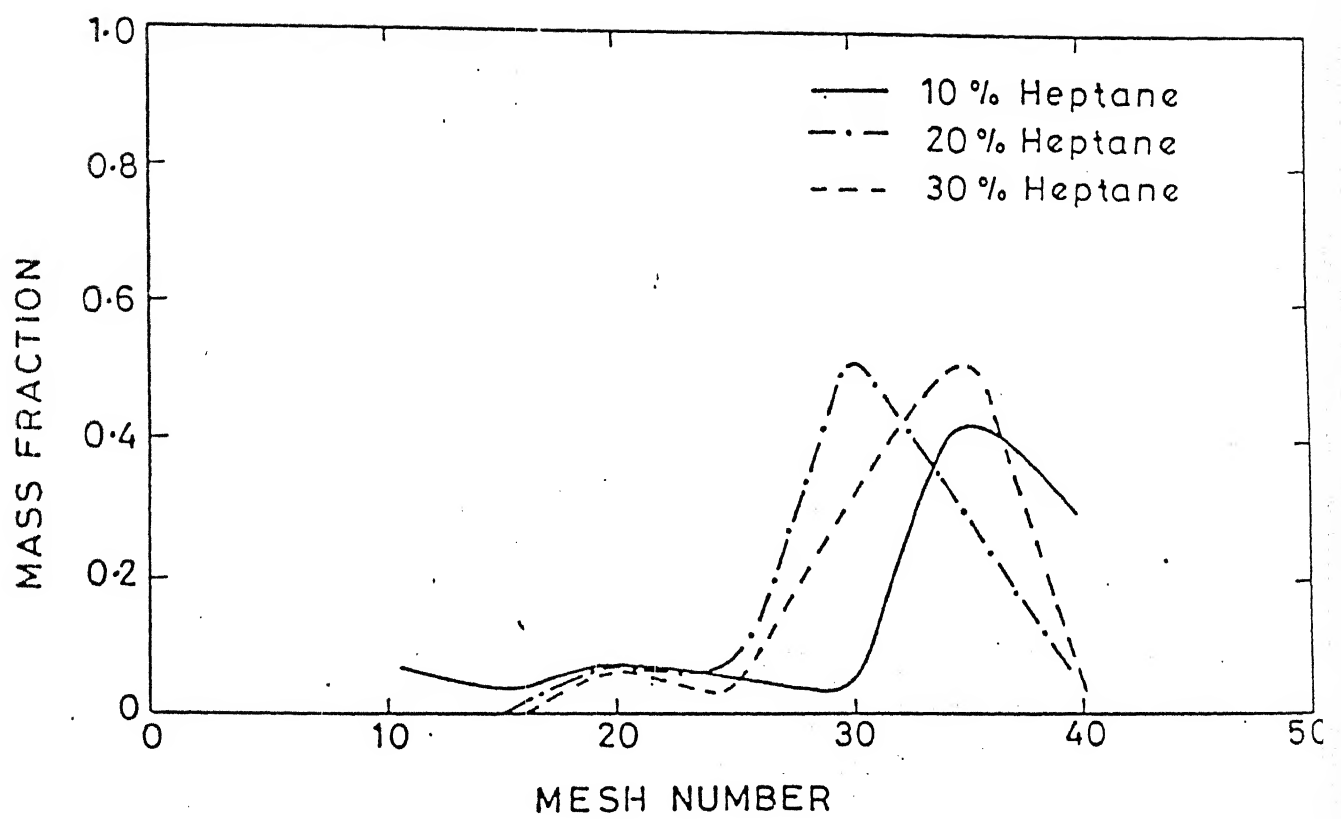


Figure 2.3 : Effect of Nature of Diluent on Particle Size Distribution of PS-DVB Resin

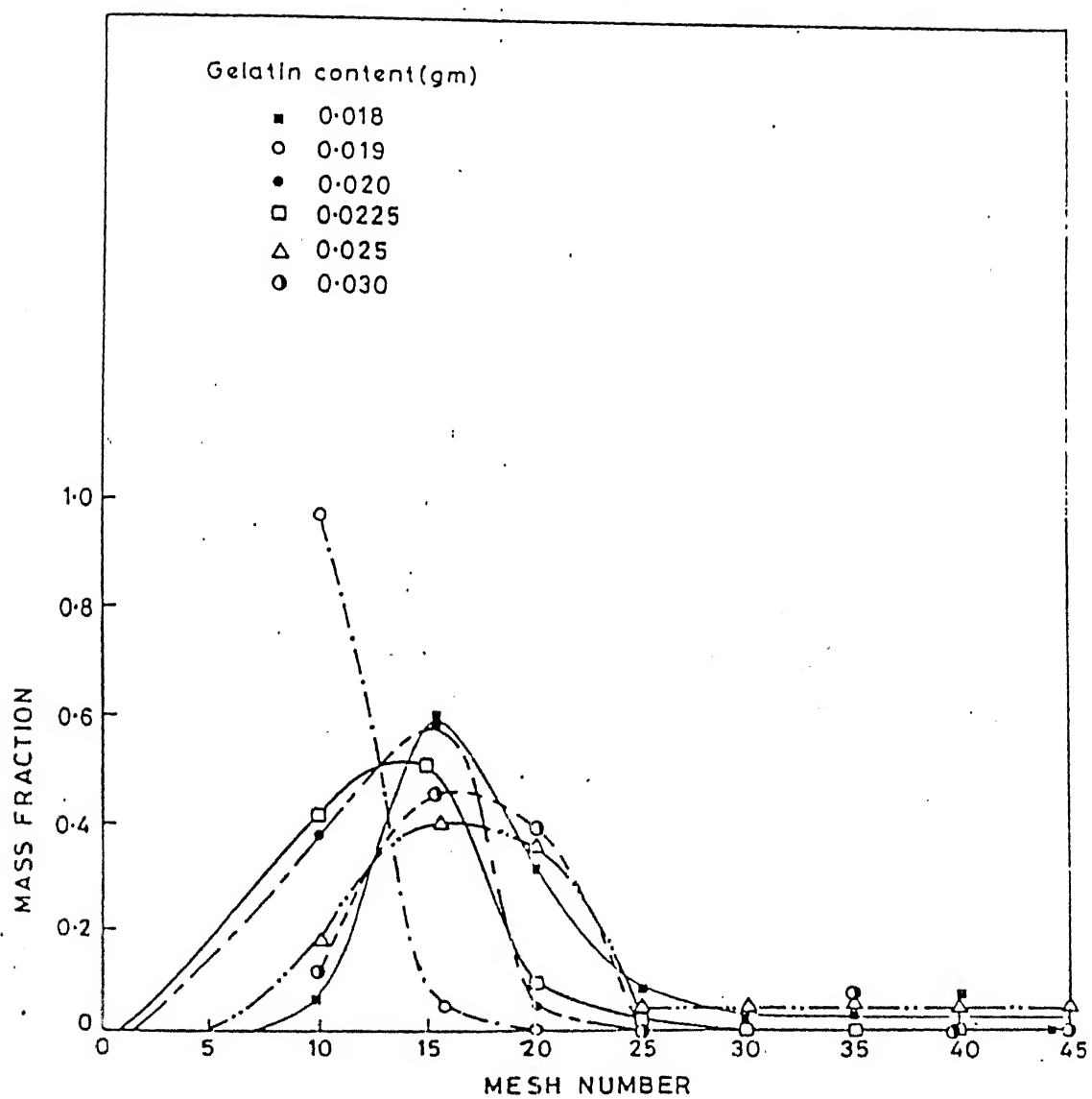


Figure 2.4 : Effect of Gelatin content on Particle Size distribution of PS-DVB Resin

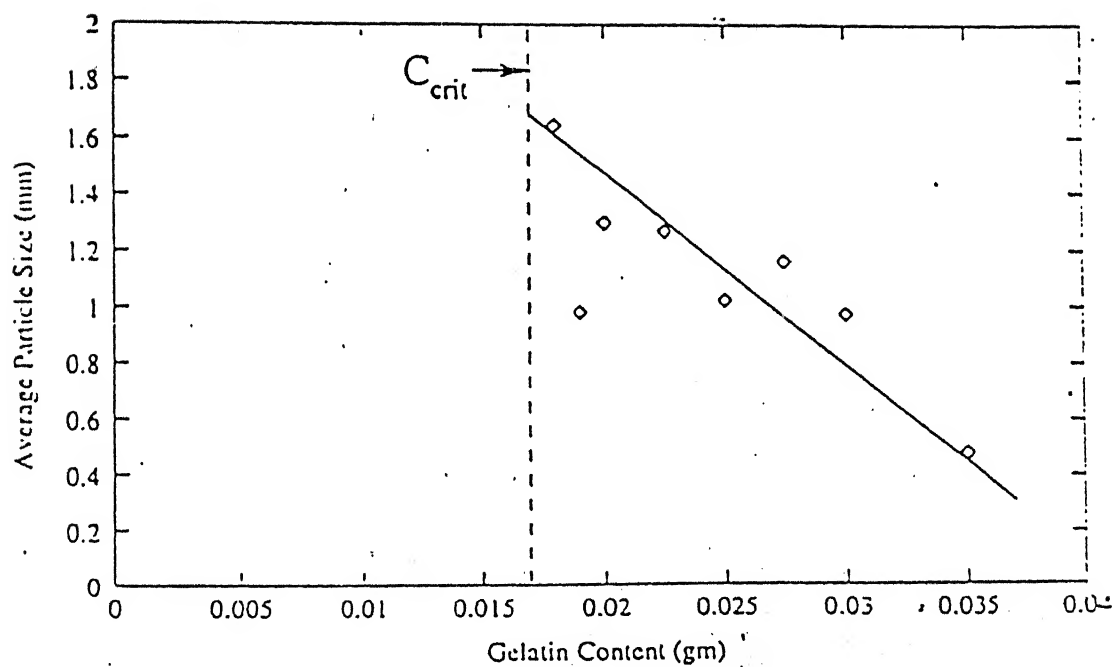


Figure 2.5 : Effect of Gelatin content on Average Particle Size of PS-DVB Resin

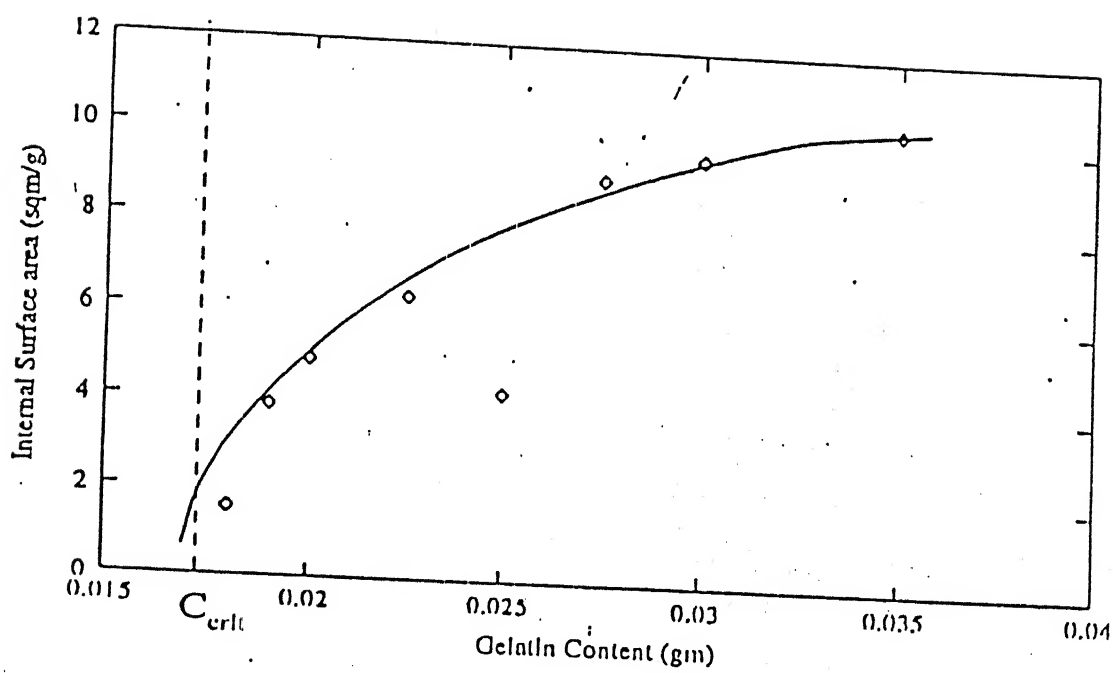


Figure 2.6 : Effect of Gelatin content on Internal Surface Area of PS-DVB Resin

(a)



(b)



(c)

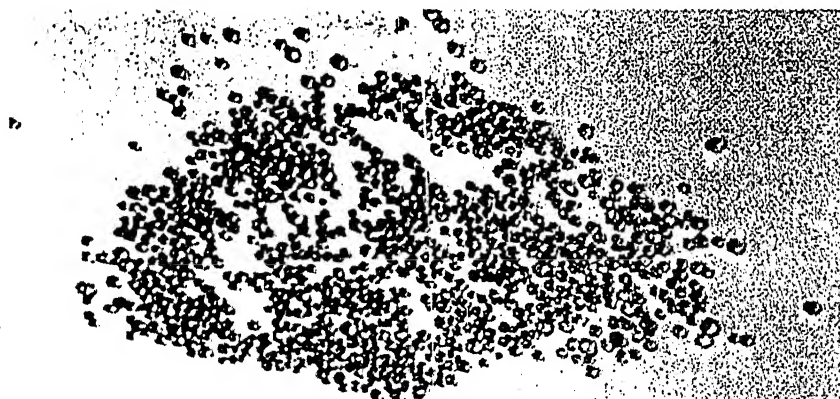


Figure 2.7 : Effect of modification on colour of PS-DVB resin

(a) Unmodified, (b) Surface Nitrated, (c) Surface Aminated

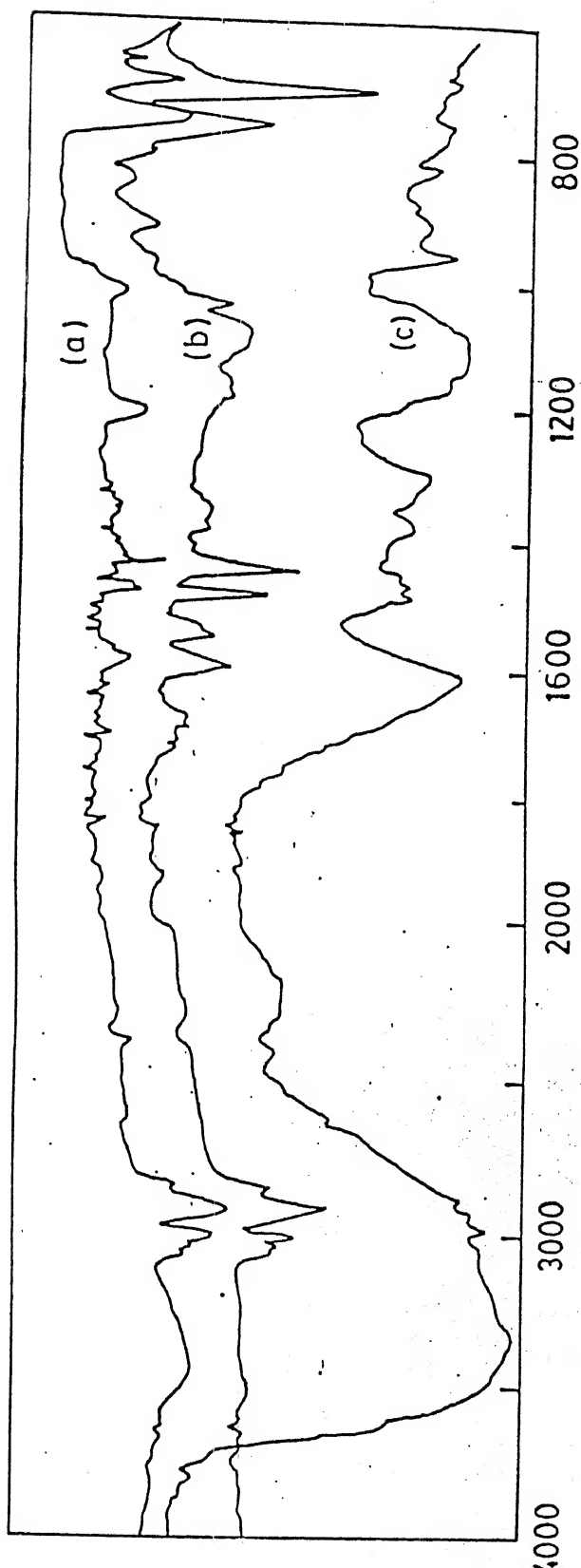


Figure 2.8 : FTIR of (a) Unmodified Resin (b) Surface Nitrated Resin and (c) Surface Aminated Resin

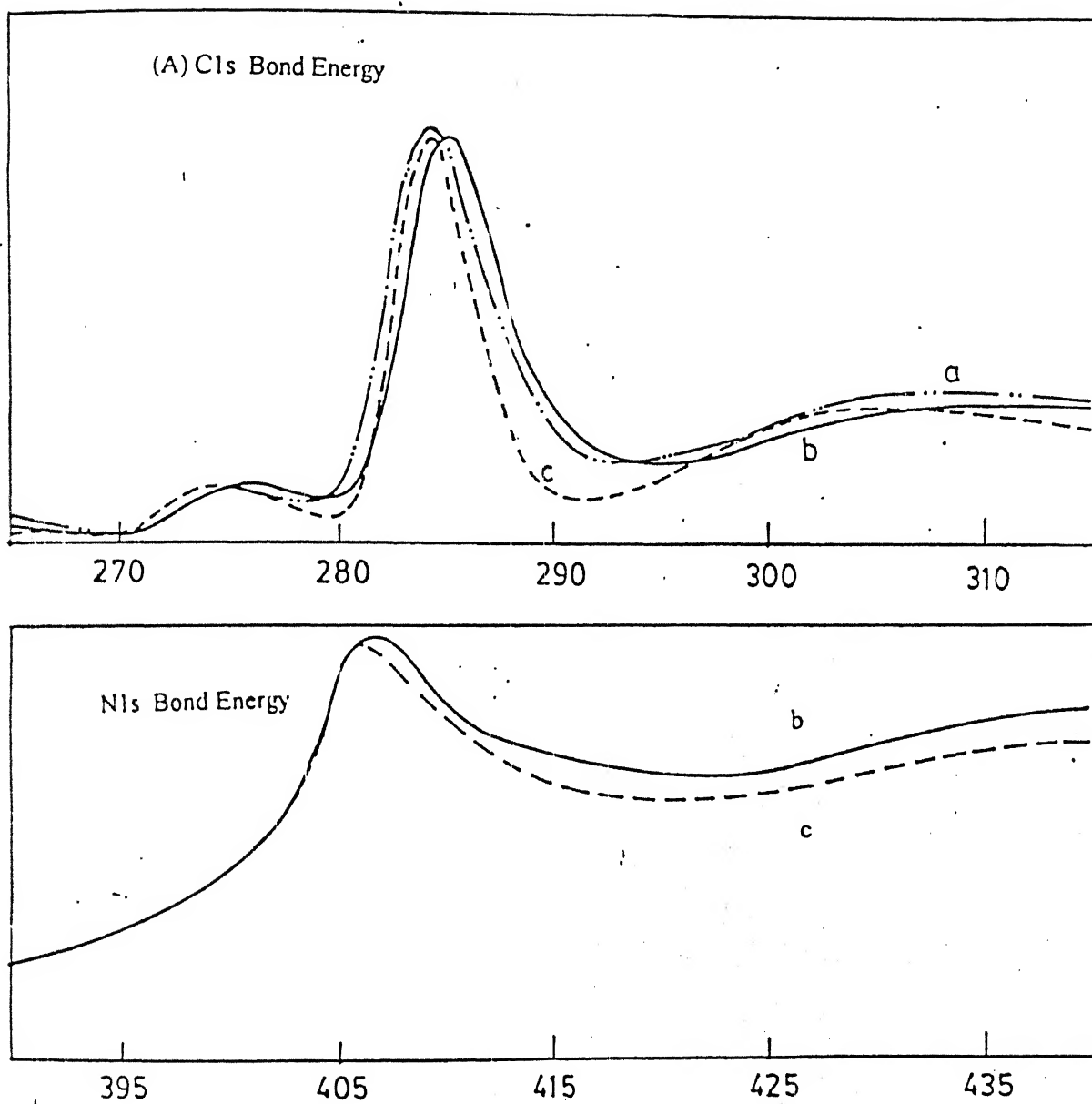


Figure 2.9 : ESCA analysis of (a) Unmodified Resin, (b) Surface Nitrated Resin and (c) Surface Aminated Resin

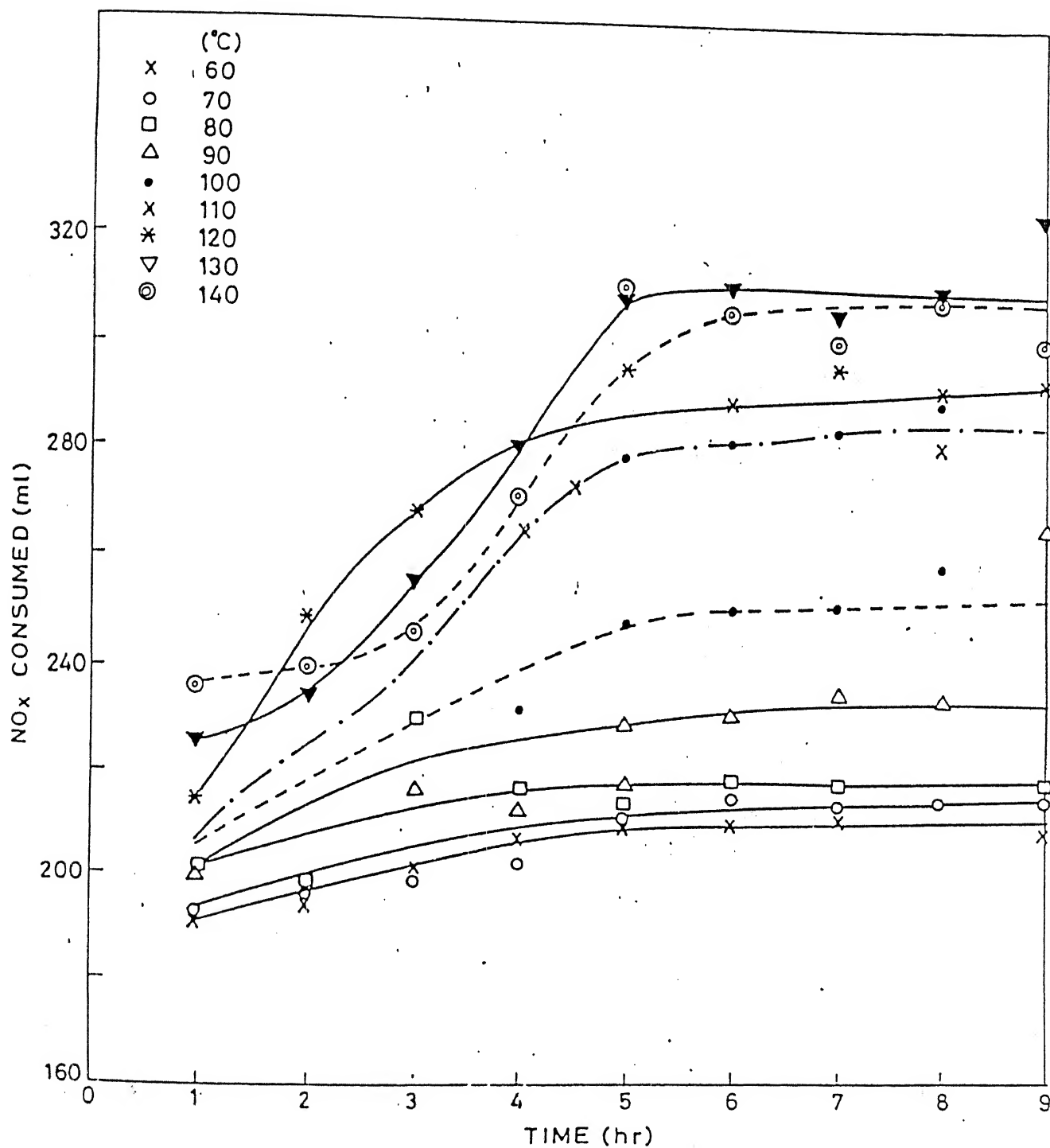


Figure 2.10 : Effect of Time and Temperature on NO_x Consumption during the Surface Nitration of PS-DVB Resin

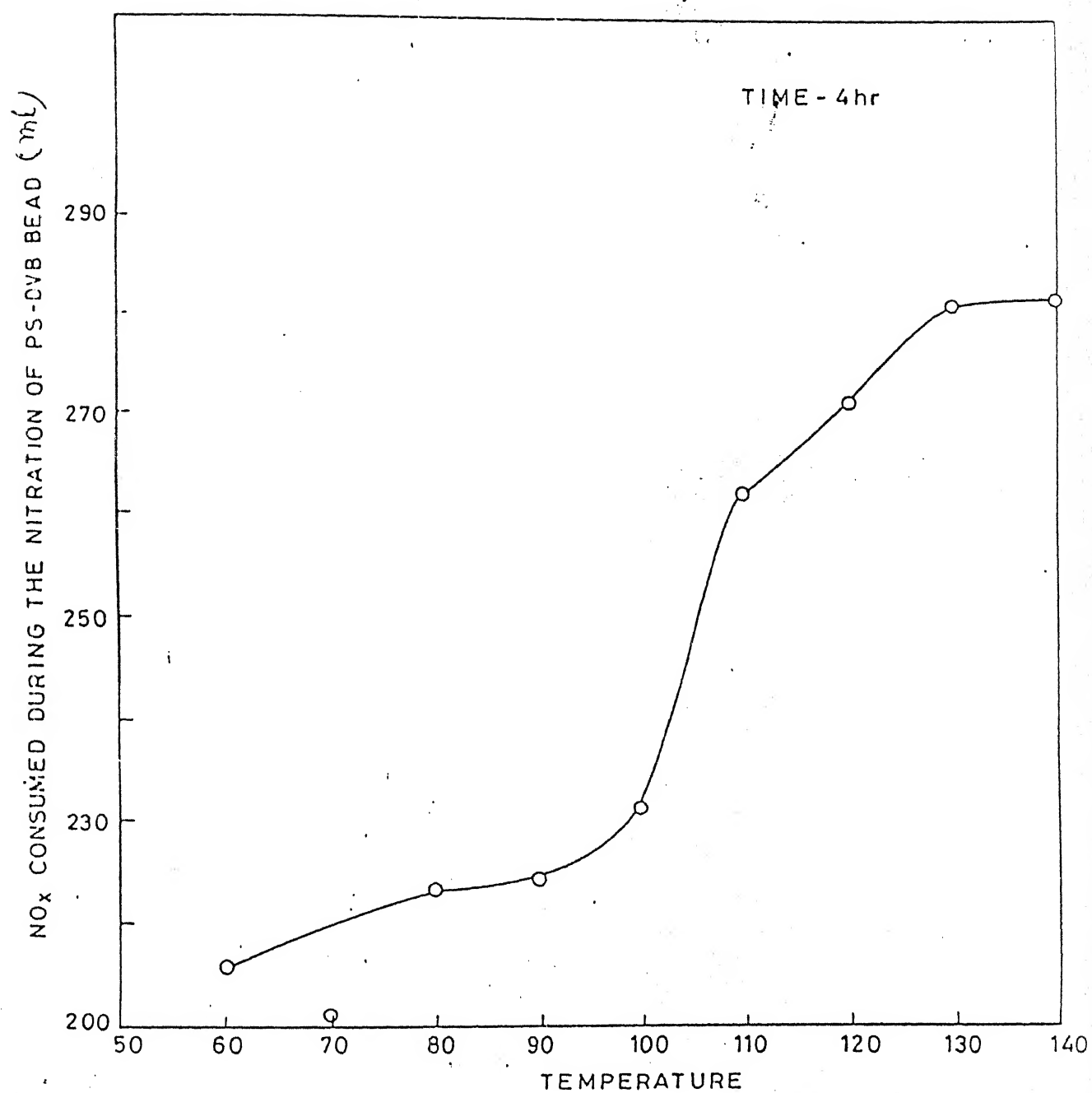


Figure 2.11: Effect of nitration temperature on NO_x consumption for PS-DVB resin

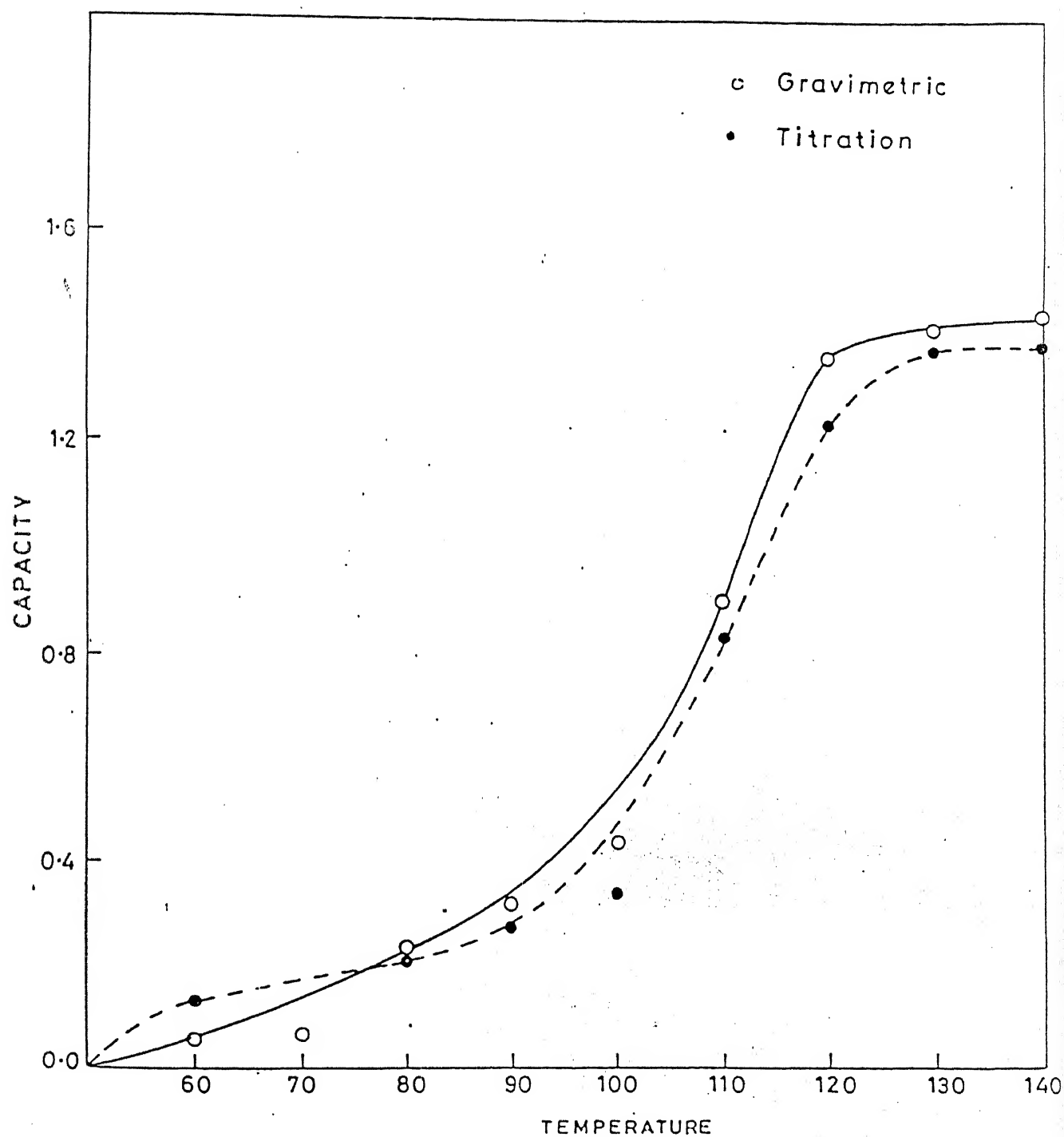
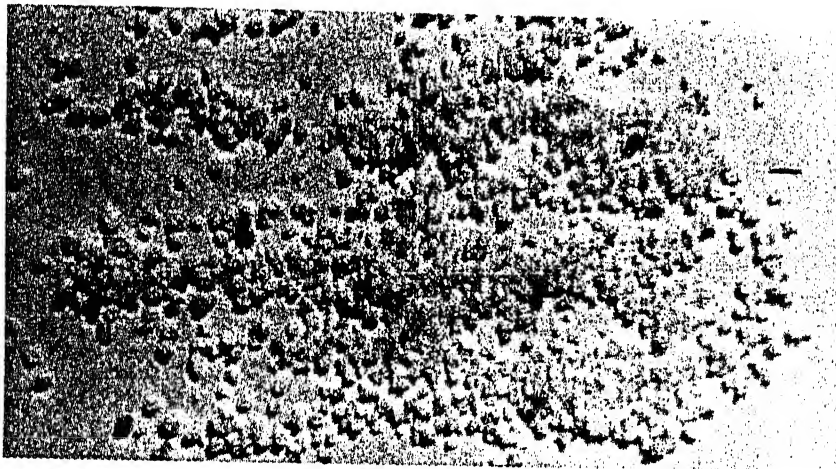


Figure 2.12 : Effect of Temperature on the Capacity of PS-DVB Resin

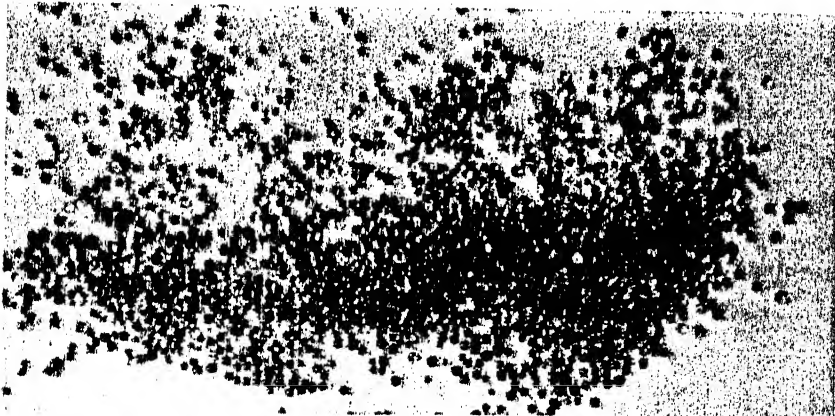
(a)



(b)



(c)



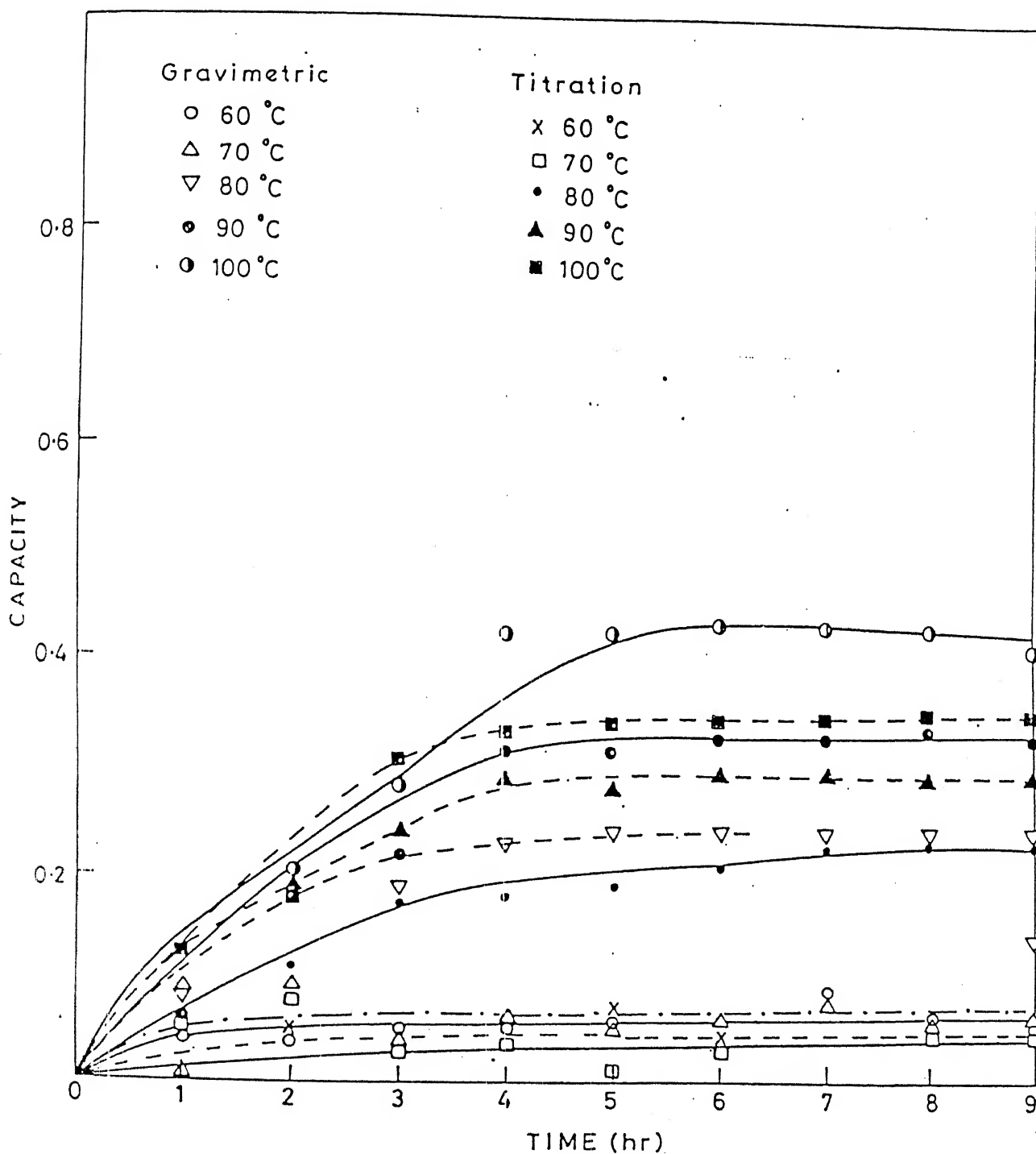


Figure 2.14 : Effect of Nitration Time and Temperature on the Capacity of PS-DVB Resin

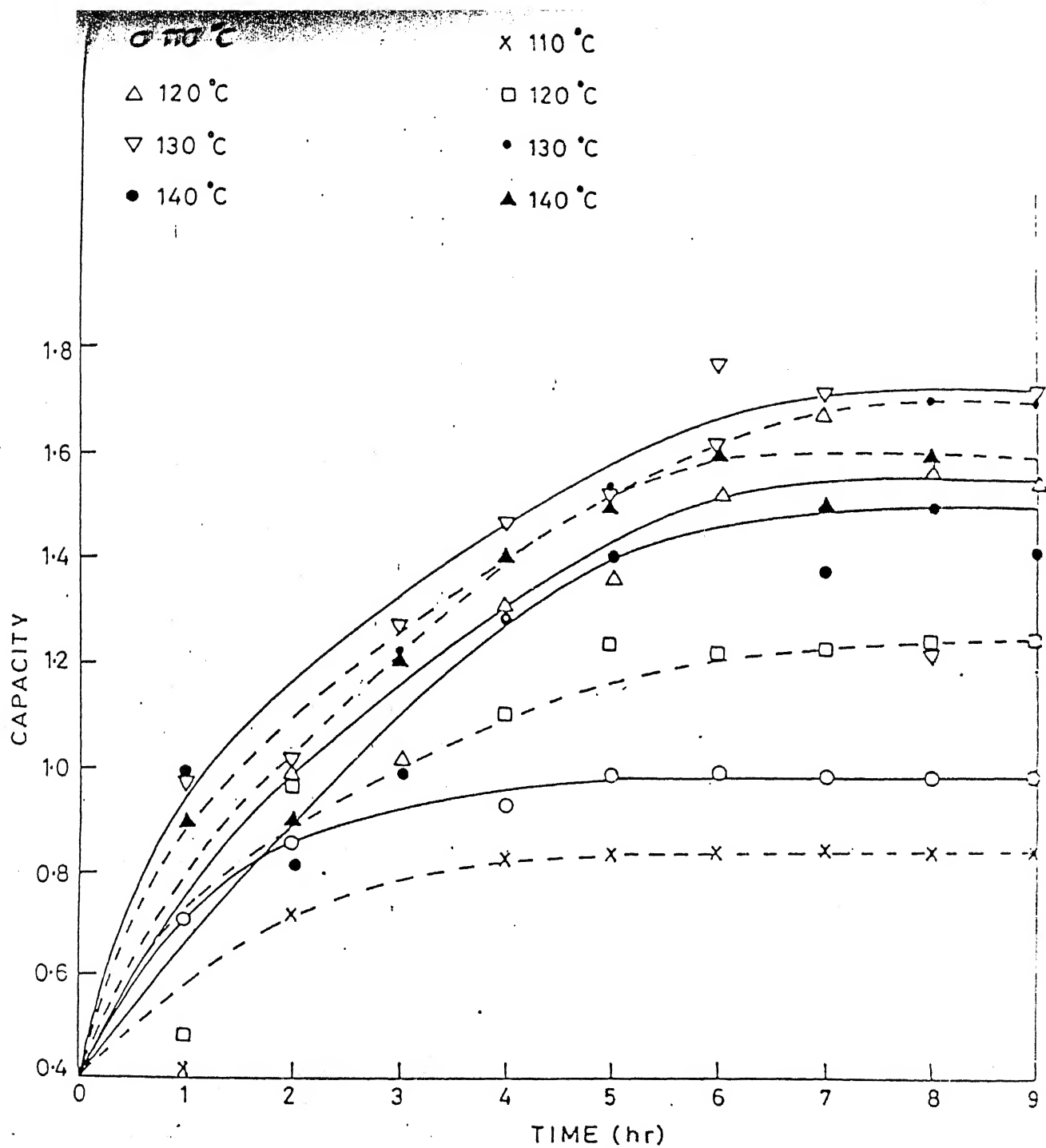


Figure 2.15 : Effect of Nitration Time and Temperature on the Capacity of PS-DVB Resin

Chapter – 3

Chemical Modification of Aminated PS-DVB Resin

3.1 Introduction

In Chapter 1, we reviewed the different modification techniques for PS-DVB resins and it was observed that for advanced applications to obtain a specific function group within the polymer matrix, the starting point has generally been the chloromethylation of PS-DVB resins. In Chapter 2, it was observed that this being a liquid phase reaction, the chloromethylation in commercial anion exchange resins was limited to within 1.00 meq Cl/g of resins and depended heavily upon the extent of penetration of chloromethyl methyl ether (CMME) into the internal pores of the copolymer PS-DVB resin. In view of this in the previous chapter we developed an entirely new and efficient gas phase nitration technique involving NO_x and their subsequent amination. Since the amine groups are more reactive, these resins can be easily utilized by further modification for more advanced applications. In this chapter, we have decided to chloroethylate the resin by reacting it with dichloroethane and study its effect upon the exchange ability of the resin.

In the previous chapter we have already determined the exchange capability of the animated resin (R-3) and it was found that during the first run, these gave high exchange of chloride ions. However, these resins cannot be regenerated by procedures recommended by ASTM standards ASTM D-2187, 2687, 3087, 3375¹¹⁰ and as a result of this in the second and subsequent runs its exchange capacity falls to a negligible value. The chloroethylation of resin is found to overcome this difficulty of regeneration and

enhance the exchange capacity of these animated PS-DVB resins (R-3). In an alternate modification scheme, the reaction of aminated resin with epichlorohydrin produces weak base anion exchange (R-6) resin and it was also found that they could then be regenerated as well as it doubles the effective anion exchange capacity. After modification of the animated PS-DVB resin (R-3) by reacting it with dichloroethane, we then prepared its ammonium and phosphonium salts using trimethyl amine, triethyl amine and triphenyl phosphine. We have examined the anion exchange ability of these modified resins and found that its capacity jumped to about 5 meq/g. In order to study the effect of extent of nitration on the final capacity of anion exchange resins, we have varied the duration of nitration systematically. We found that for short times, the capacity rises quickly first due to generation of increased sites; however for longer times there appears to be blocking of internal pores (and hence reduction of surface areas) as a result of which the exchange capacity falls. Experiments reveal that best results are obtained for about five hours of nitration.

In order to investigate the cause of this high exchange capacity of the anion exchange resins prepared through nitration method, we have determined their water uptake characteristics and compared this with commercially available resins. We have saturated the resin with water by refluxing them with distilled water for four hours and then subjected them to following different drying procedures sequentially.

- (1) drying in oven at $100 \pm 5^\circ\text{C}$ for 12 hours
- (2) drying in a vacuum dessicator maintained over P_2O_5 at 100°C and a vacuum of 750 mm.
- (3) Drying in dessicator maintained over P_2O_5 at ambient conditions for six months.

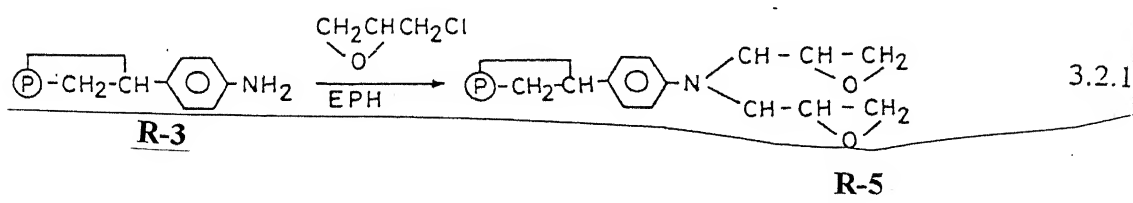
The unmodified resin (R-1) is found to imbibe 8.59% moisture, but loses it completely by stage 1 drying. Commercial Dowex anion exchange resin had a total of 43% moisture content out of which 11.4% was lost by procedure (1) while the remainder 32.13% was completely removed by procedure (2). As opposed to this, the anion exchange resin prepared through nitration method, the loss of moisture by procedures (1) and (2) was within 5% only while complete drying required procedure (3) and time period of about six months. In this chapter we have presented a systematic study of solution characteristics of the resin with the duration of nitration as a parameter and showed that the solvation ability of the PS-DVB resin prepared in this chapter is considerably higher.

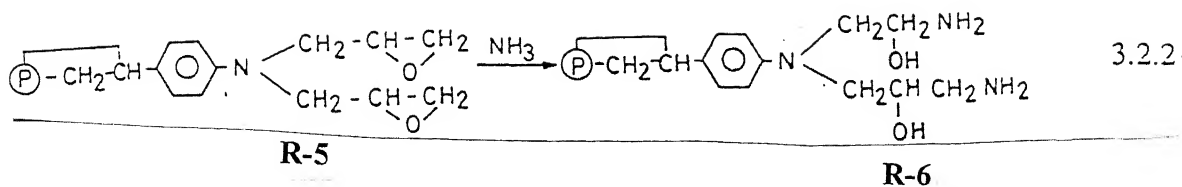
3.2 Experimental Procedure:

3.2.1 Modification of Aminated PS-DVB Resins (R-3) with Epichlorohydrin:

The aminated PS-DVB resin (R-3) is refluxed with 50ml of 5% v/v of epichlorohydrin in ethanol for four hours. The resins are then filtered washed and dried. The dried resin is then reacted with ammonia water to get amine group on the polymer matrix. There is a significant change in colour of the resin due to modification epichlorohydrin as shown in Figure 3.1.

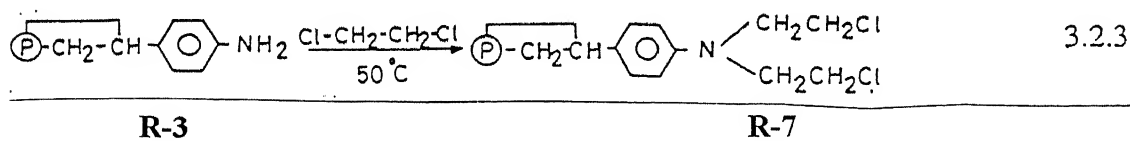
The reaction occurring is as follows:





3.2.2 Modification of Aminated PS-DVB Resin with Dichloroethane:

Approximately 1.5 g of aminated PS-DVB resin is refluxed with 50ml 2% v/v solution of dichloroethane in ethanol for four hours. After the completion of the reaction, the resin is filtered, washed and dried. Higher concentration of dichloroethane are avoided because the resins become sticky and lumps are formed. No visible change in colour is observed. The reaction occurred as follows:

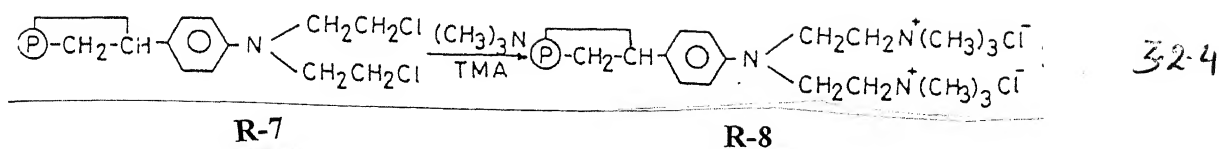


Now this modified polymer readily forms an ammonium salts with trimethylamine, triethylamine and triphenyl phosphine.

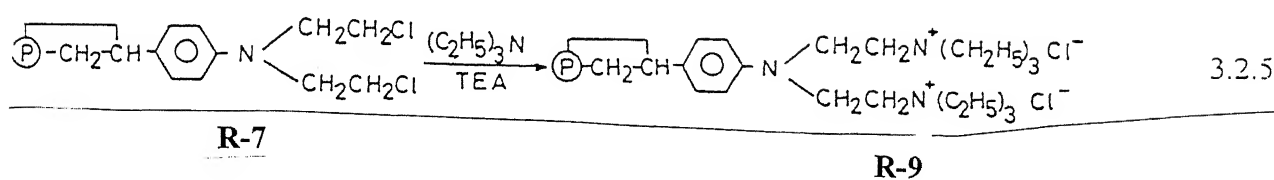
3.2.3 Modification of Chloroethylated PS-DVB Resin with Trimethylamine, Triethylamine and Triphenylphosphine

After modification with dichloroethane the dried resin is treated with 20ml of 5% v/v trimethylamine in ethanol. The entire content is refluxed for four hours. In an another set saturated solution of triphenylphosphine is prepared in ethanol and 20 ml of this saturated solution is refluxed with 1.5 g of chloroethylated polymer resin for four hours. After completion of reaction, the resin is washed and dried and are ready for examining the anion exchange capability. The reaction occurring during the above treatment can be written as:

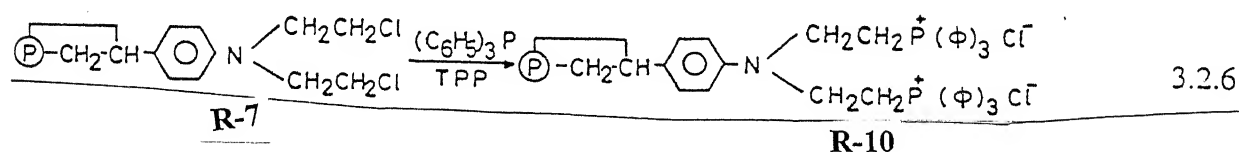
(i) Reaction with trimethylamine:



(ii) Reaction with triethylamine:



(iii) Reaction with triphenylphosphine:



After treatment with trimethylamine, triethylamine and triphenylphosphine, the resin is examined for functional group attachment and their anion exchange capacity by ASTM procedure, given in Chapter 2.

3.3 Determination of Equilibrium Water Content:

Ion exchanger^{12,111} usually absorbs water and swell due to their solvation ability.

This swelling occurs upto an extent that an equilibrium is attained. We followed the

following experimental procedure to determine this and to assess the solvation ability of the resin prepared in this chapter.

- (a) Saturation of Polymer Resin with Moisture: Approximately 1.5 g of resin which has already been dried in dessicator for 6 months is weighed and placed in a standard joint conical flask. This resin is refluxed with 100ml of distilled water for four hours. The resin is separated and dried from the water adhering to it with the help of filter papers.
- (b) Oven Drying: The surface dried resins are once again weighed which is wet mass of the resin. In order to assess how strongly water is solvated by the resin have carried out drying in two stages. In the first one, the resins are placed in an oven maintained at $105 \pm 2^{\circ}\text{C}$ for four hours and weight is determined after this. The mass of water lost by this procedure is called Shell 1 moisture.
- (c) Vacuum Drying: In the second stage of drying, the resin from the oven is subjected to vacuum drying at 100°C for twenty four hours at 750mm Hg vacuum. The mass of the moisture lost by this procedure has been termed as Shell 2 moisture.
- (d) Vacuum drying for six months at ambient temperature under P_2O_5 : The resin obtained from stage 2 drying is stored in a vacuum dessicator for six months. The moisture lost this way has been called as Shell 3 moisture.

The first two stages of drying have been chosen commercial resin losses moisture completely. The unmodified resin loses the absorbed water completely after first stage of drying while the commercial Dowex strong base anion exchange resins (obtained by

chloromethylation) lose 11.4% absorbed water after first stage while the remaining 32.13% is lost by second stage drying.

3.4 Results and Discussion:

In Chapter 2, it was observed that the capacity of aminated PS-DVB (R-3) resin goes down to zero during the first regeneration cycle and cannot be further regenerated. This was explained by the fact that the aniline moiety of the modified resin had very low pK value and it was felt that on its further modification, shortcoming of the resin would be removed. In this chapter these aminated PS-DVB(R-3) resins are further modified and it is shown that these resins could then be regenerated by the procedure given in ASTM and ISI¹¹⁰ standards. In our experimentation we determined the exchange capacity of a given resin in two consecutive runs and these capacities were found to be close to each other within the experimental errors.

In order to make resins regenerable, we first modified the aminated PS-DVB resins with epichlorohydrin to get weak base anion exchange (R-6) resin. Experimentally, we have shown that the exchange capacity is doubled which implies that two molecules of epichlorohydrin are attached to the amine group. The reaction is extremely simple, occurs smoothly and is associated with slight colour change of the resin as shown in Figure.3 1. In preparing these resins, the parameter that was varied systematically was the duration of nitration, keeping the other factors like time of amination and time of reaction with epichlorohydrin as invariant. Experiments also confirm that the duration of nitration has considerable effect upon the final capacity of the resin and the results on the exchange capacity of the resin have been plotted in

Figure.3.2. For each point in this graph, at least two consecutive runs were made using both gravimetric and titration methods for evaluation of the capacity of the resin. For each experimental run, it took one days for nitration, one day for amination, one day for modification with epichlorohydrin and four days for determination of the exchange capacity. All intermediate steps and details of various runs of Figure.3.2 are summarized in Table 3.1. Figure 3.2 shows that for short time of nitration, the capacity of the resin rises which is expected. This is expected because the increasing duration of the nitration increases the number of sites of functional groups on the resin. However for longer times, there is slight fall which perhaps indicates blocking of internal pores and consequent reduction of internal surface area. It may be recalled that in chapter 2, directly aminated resins (which do not undergo regeneration) give a maximum capacity of 1.4 meq/g whereas the maximum capacity of the epichlorodhydrin (R-6) resin (which can be regenerated) is 2.6 meq/g which is approximately twice that of the directly aminated resins. This results may not be surprising because for amine group generated in directly aminated resins (of chapter 2, Fig.2.3), two amine groups are created on the modified resin as seen in eqn. 3.2.2.

In an alternate modification scheme, the directly aminated resins (R-3) of chapter 2 were refluxed with dichloroethane and then modified by trimethylamine (TMA), triethylamine (TEA) and triphenylphosphine (TPP). In order to confirm that two dichloroethane molecules are attached, we have refluxed the modified resin for four hours. The chloride ion attachment have been determined by precipitation from silver nitrate solution and was determined to be 2.65 meq/g. The capacity of these strong base resins have been determined by the similar ASTM and ISI procedure and the results are

given in Table 3.2, 3.3 and 3.4 and in Figs. 3.3, 3.4 and 3.5. For each experimental data shown in these figures the determination of exchange capacity was similarly performed twice for a given resin in at least two consecutive runs in order to show that the resins can be regenerated and can be used as an anion exchange resin. The parameter that was systematically varied was once again the duration of nitration and every sample of the resin were aminated, reacted with dichloroethane identically. The results show that the modified strong base PS-DVB resins have a maximum capacity of around 5 meq/g in all three cases which occurs after 5 h of nitration and the slight fall in capacity occurs for duration more than this which can be explained to occur because of blocking of pores.

In the chapter 2, the capacity for directly aminated weak base PS-DVB resin (R-3) was found to be 1.4 meq/g, which drops to 0.1 meq/g in the second run and can not be regenerated. After modification of these resin with dichloroethane the capacity is found to be about five times this value which does not fall in subsequent exchange cycles. We have determined the capacity over ten cycles of ion exchange and found that the modified strong base resin can be regenerated by ASTM (and ISI) procedures and therefore can be used as anion exchange resin and can replace the commercial resin which has a capacity of 1 meq Cl/g. The jump in the capacity of the modified strong base anion exchange cannot be explained by simple count of exchanging sites alone. This is because if this was the fact, then the modification with epichlorohydrin would have been equivalent to the modification by dichloroethane but this was not found to be the case. The figure 3.3 to 3.5 show the effect of change in the counter ion from trimethylamine triethylamine triphenylphosphine and are found to have similar trend in all these cases. From these we observed that initially there is a rise in capacity and undergoes a maximum value

followed by a gradual and slow fall eventually attaining an asymptotic value. This is because for small duration of nitration, the internal pores are large enough for the ion exchanging liquid to enter the internal pores with relatively smaller diffusional resistance. However due to the modifications with trimethylamine, triethylamine and triphenylphosphine, some of these pores are blocked and are not available for exchange of ions. As the degree of amination increases for large nitration times, the sites of modification also increases and the fall in the capacity is explained by the blockage of these pores. Triphenylphosphine having the large molecule (molecular weight 262), blocks the pores of the resins more quickly compared to triethylamine (molecular weight 59) and triethylamine (molecular weight 101). From the capacity results shown in Table 3.2 to 3.4, it is observed that with triphenylphosphine as the counterion, the maximum in capacity occurs earlier in time of nitration.

In order to understand the five time increase (compared to commercially available strong base exchangers) in capacity of PS-DVB, resin after the modification by dichloroethane (R-7), one must consider the exchange equilibrium. The resin can be represented by a crosslinked network of chains which consists of rigid, rod-shaped segments that carry charges. When the resin is immersed in a water solution of electrolytes, the matrix of the polymer gel stretches like elastic springs to accommodate the water as well as the electrolytes. The study of ion exchange resins for separation has been going on for over fifty years and there has been a continued effort to synthesize exchangers of higher capacity. These studies have revealed that higher capacities are favoured by (a) low degree of crosslinking, (b) strong solvation tendency of the fixed

ionic groups, (c) large and strongly solvated counter ion, (d) low valence of counter ion (e) complete dissociation in the resin and (f) swelling due to water of hydration.

The commercially available anion exchange resin always have “free” solvent and solvent bound in the form of solvation shell. The water uptake by an initially dry resin is accompanied by swelling of the former. Experiments with these resins have shown that the free water can be removed either by centrifugation or by oven drying whereas the solvation shell moisture can be removed under vacuum and temperature of 100°C for 24 hours. The experiments with our chloroethylated PS-DVB resins reveal that water is quite differently bound and application of high vacuum and temperature alone are not sufficient to characterize solvation shells.

We first prepared anion exchange resins for different time duration of nitration and aminated, reacted with dichloroethane in the usual way as described earlier. We then put these in a dessicator (containing P_2O_5) for the six months for drying at ambient temperature and vacuum of 750 mm. We determined the mass of these and called these as dry mass. We subsequently boiled them with distilled water for four hours and determined their masses after drying them with filter paper. These resins were dried under the following three drying conditions.

- (a) The resins are dried in oven for four hours. This is regarded as free moisture or first shell moisture

- (b) The resins obtained from (a) are dried for twenty four hours in a dessicator at 750mm Hg vacuum and 100°C temperature. This represents as second shell moisture,
- (c) The resin obtained from (b) is put in a dessicator (containing P_2O_5) for the next three months under vacuum of 750 ml Hg till the original dry mass of the resin obtained. This represents as third shell moisture.

For example, for Dowex anion exchange resin 11.4% moisture was lost in oven drying thus constituting first shell moisture while the remainder 32.13% moisture was lost in the vacuum drying at 100°C in twenty four hours this being the second shell moisture. There was nothing remaining as the third shell moisture

In our case as seen in Table 3.5, the unmodified PS-DVB resin (R-1) retains a total of 8.59% as first shell moisture and none as shell 2 and 3 moistures and this result is expected because the unmodified resins are hydrophobic in nature. However in the case of strong base chloroethylated PS-DVB resin (R-8, R-9, R-10), the first shell moisture content first increases as the extent of nitration increases but it falls for larger times of nitration this way having a maxima and low asymptotic value. This reduction in the shell 1 occurs with simultaneous fall in shell 2 moisture and increase in the shell 3 moisture due to increase in nitration. However for large times of nitration, moisture in shell 3 is held with greater energy of interaction and the amount of water held increase only slightly as seen in Tables 3.6 to 3.8. We have also examined the effect of the counter ions used upon the solvation ability of the resin. The same trend is observed when the counter ion are present and results for trimethylamine, triethylamine and

triphenylphosphine counter ions modified chloroethylated PS-DVB resin are shown in these figures. In the case of triphenylphosphine counter ion, a broad maxima in the shell 1 moisture content is obtained. The initial rise in these curves is similarly explained on the basis of more number of anions available on the surfaces of modified resin. The sharpness in the fall is the highest for aminated resins while curves for triphenylphosphine counter ion, are broad. The observed trend can be represented by the following series : aminated (R-3) resin > TMA modified (R-8) resin > TEA modified (R-9) resin > TPP modified (R-10) resin.

Figs.3.6 and 3.7 show the effect of the duration of nitration on the second and the third shell moistures and it is seen that the first and the second shell falls to give the increased third shell moisture for larger times of nitration. This clearly indicates that moisture in the resin prepared by us is held with increased interactive forces, this way giving more solvation and evidently our resins are more hydrophilic. In Figure3.7 the asymptotic amount of the third shell moisture is formed to depend upon the counter ion used and is the largest for TPP counter ion. For aminated resin (R-3) where the counter ion is NH_4^+ , for short duration of nitration, the third shell moisture is the smallest first, but for large times of nitration, it surpasses the values for TMA and TEA counter ions. It has been already pointed out that solvation energy affects the capacity of the resin to a great extent and the increased capacity of the resin developed by us may as well as due to this increased solvation of moisture in the polymer resins.

3.5 Conclusions:

The weak base aminated PS-DVB resin (R-3) prepared in Chapter 2 could not be regenerated using ASTM (and ISI) procedure and in order to overcome this difficulty, we decided to further modify these resins. The resin modified by epichlorohydrin (R-5) gives weak base anion exchange resin and has a capacity of approximately twice of the aminated resin. This suggests that for every amine group produced by nitration, two molecules of epichlorohydrin are reacted.

Considerably more interesting results are obtained when the aminated resins are reacted with dichloroethane to give chloroethylated resins (R-8, R-9, R-10). The measure of surface chloride clearly suggest two dichloroethane molecules react with every amine groups. The change from chloromethylene to chloroethylation increases exchange capacity to five times the value of commercial resin. In order to assess the difference in the solvation ability of chloroethylated resins, we devised three stages of moisture drying procedure. We showed that unmodified resin had only shell 1 moisture while commercial strong anion exchange resin has shell 1 and 2 moisture. As opposed to this, the chloroethylated strong base resin has largely shell 3 moisture and this increased monotonically with the duration of nitration..

Table 3.1
Capacity of Epichlorohydrin Modified PS-DVB Resins (R-6)

Duration of Nitration (hr)	Gravimetric Estimation				Titration		
	Amount of resin (g)	Wt. of ppt. for two conc. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of resin (g)	Titre Value (ml)	Capacity (mmoles/g)
1	0.7639	(i) 0.0260 (ii) 0.0152	(i) 0.237 (ii) 0.139	0.188	0.3632	4.9	0.275
2	0.6327	(i) 0.0680 (ii) 0.0573	(i) 0.749 (ii) 0.631	0.690	0.3978	4.7	0.754
3	0.4799	(i) 0.0752 (ii) 0.0698	(i) 1.092 (ii) 1.014	1.053	0.4117	4.5	1.214
4	0.5631	(i) 0.0940 (ii) 0.1575	(i) 1.163 (ii) 1.949	1.556	0.5601	3.9	1.964
5	0.3921	(i) 0.0978 (ii) 0.1203	(i) 1.739 (ii) 2.138	1.939	0.4738	3.8	2.533
6	0.6118	(i) 0.2395 (ii) 0.1820	(i) 2.728 (ii) 2.073	2.401	0.3119	4.1	2.886
7	0.6978	(i) 0.2967 (ii) 0.2182	(i) 2.963 (ii) 2.179	2.571	0.4218	4.0	2.371
8	0.6841	(i) 0.2689 (ii) 0.9093	(i) 2.739 (ii) 2.132	2.436	0.4691	3.8	2.558
9	0.7128	(i) 0.2088 (ii) 0.2198	(i) 2.041 (ii) 2.149	2.095	0.4472	4.1	2.013
10	0.6569	(i) 0.2478 (ii) 0.2112	(i) 2.629 (ii) 2.241	2.435	0.4811	3.9	2.286
11	0.6036	(i) 0.1673 (ii) 0.1487	(i) 1.932 (ii) 1.717	1.825	0.4012	4.2	1.994
12	0.6881	(i) 0.2104 (ii) 0.2604	(i) 2.131 (ii) 2.637	2.384	0.4649	3.9	2.366

Table 3.2
Capacity of TMA Modified PS-DVB Resins(R-8)

Duration of Nirration (hr)	Gravimetric Estimation				Titration		
	Amount of resins (g)	Wt. of ppt. for two consc. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of resins (g)	Titre Value (ml)	Capacity (mmoles/g)
1	0.3848	(i) 0.1975 (ii) 0.2046	(i) 3.58 (ii) 3.71	3.64	0.3743	4.0	2.67
2	0.44456	(i) 0.2692 (ii) 0.2529	(i) 4.22 (ii) 3.96	4.09	0.4494	3.5	3.33
3	0.6823	(i) 0.4390 (ii) 0.4123	(i) 4.49 (ii) 4.23	4.36	0.6761	3.0	2.96
4	0.6200	(i) 0.4336 (ii) 0.4224	(i) 4.89 (ii) 4.76	4.83	0.6206	3.1	3.06
5	1.2288	(i) 0.3512 (ii) 0.3656	(i) 1.79 (ii) 2.08	1.94	1.2351	2.8	1.78
6	0.5012	(i) 0.3810 (ii) 0.3621	(i) 5.31 (ii) 4.49	4.90	0.5028	3.0	3.90
7	0.7143	(i) 0.3205 (ii) 0.3225	(i) 3.13 (ii) 3.16	3.14	0.7107	3.1	2.67
8	0.4390	(i) 0.2500 (ii) 0.2421	(i) 3.98 (ii) 3.85	3.92	0.4285	3.5	3.50
9	0.4231	(i) 0.2115 (ii) 0.2262	(i) 4.49 (ii) 3.73	3.61	0.3906	4.0	2.56
10	0.4073	(i) 0.1570 (ii) 0.1689	(i) 2.69 (ii) 2.89	2.79	0.3797	4.1	2.37
11	0.6382	(i) 0.2280 (ii) 0.2173	(i) 2.49 (ii) 2.38	2.44	0.6132	3.7	2.12
12	0.4181	(i) 0.1195 (ii) 0.1283	(i) 2.00 (ii) 2.14	2.07	0.4074	3.9	2.70

Table 3.3
Capacity of TEA Modified PS-DVB Resins(R-9)

Duration of Nitration (hr)	Gravimetric Estimation				Titration		
	Amount of resins (g)	Wt. of ppt. for two conc. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of resins (g)	Titre Value (ml4)	Capacity (mmoles/g)
1	0.3913	(i) 0.1285 (ii) 0.1126	(i) 2.29 (ii) 2.01	2.15	0.4040	4.3	1.73
2	0.4346	(i) 0.2173 (ii) 0.1998	(i) 3.49 (ii) 3.21	3.35	0.4004	3.9	2.74
3	0.7063	(i) 0.3832 (ii) 0.3641	(i) 3.79 (ii) 3.60	3.70	0.6467	3.2	2.78
4	0.5400	(i) 0.3217 (ii) 0.3145	(i) 4.16 (ii) 4.07	4.12	0.5874	3.2	3.06
5	0.7000	(i) 0.5105 (ii) 0.5202	(i) 5.09 (ii) 5.19	5.14	0.7505	2.5	3.33
6	0.7692	(i) 0.4390 (ii) 0.4287	(i) 3.99 (ii) 3.89	3.94	0.7075	3.0	2.83
7	0.7572	(i) 0.5291 (ii) 0.5266	(i) 4.88 (ii) 4.86	4.87	0.7428	2.6	3.23
8	0.3000	(i) 0.2145 (ii) 0.2046	(i) 5.00 (ii) 4.76	4.88	0.2992	4.1	3.01
9	0.6539	(i) 0.4704 (ii) 0.4421	(i) 5.03 (ii) 4.72	4.88	0.6814	2.9	3.08
10	0.3755	(i) 0.2616 (ii) 0.2309	(i) 4.87 (ii) 4.29	4.58	0.3745	3.8	3.20
11	0.7206	(i) 0.3303 (ii) 0.3179	(i) 3.20 (ii) 3.08	3.14	0.7292	3.3	2.33
12	0.7393	(i) 0.3203 (ii) 0.3315	(i) 3.02 (ii) 3.13	3.08	0.7361	3.2	2.44

Table 3.4
Capacity of TPP Modified PS-DVB Resins (R-10)

Duration of Nitration (hr)	Gravimetric Estimation				Titration		
	Amount of resins (g)	Wt. of ppt. for two consec. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of resins (g)	Titre Value (ml4)	Capacity (mmoles/g)
1	0.4740	(i) 0.1690 (ii) 0.1700	(i) 2.49 (ii) 2.51	2.5	0.4662	4.1	1.93
2	0.4323	(i) 0.2102 (ii) 0.1988	(i) 3.40 (ii) 3.21	3.31	0.4330	3.8	2.77
3	0.4312	(i) 0.2116 (ii) 0.2678	(i) 3.43 (ii) 4.34	3.89	0.4302	3.7	3.02
4	0.6026	(i) 0.3918 (ii) 0.3602	(i) 4.54 (ii) 4.18	4.36	0.6367	3.0	3.14
5	0.4232	(i) 0.3025 (ii) 0.3226	(i) 4.99 (ii) 5.33	5.16	0.4144	3.4	3.86
6	0.4422	(i) 0.2902 (ii) 0.2376	(i) 4.58 (ii) 3.75	4.17	0.4564	3.0	2.49
7	0.7997	(i) 0.4375 (ii) 0.4132	(i) 3.82 (ii) 3.61	3.72	0.8027	2.8	2.95
8	0.8208	(i) 0.5033 (ii) 0.4945	(i) 4.28 (ii) 4.21	4.25	0.7452	2.6	3.20
9	0.7454	(i) 0.4688 (ii) 0.4275	(i) 4.39 (ii) 4.01	4.20	0.7476	3.0	2.67
10	0.7459	(i) 0.4266 (ii) 0.3944	(i) 3.99 (ii) 3.69	3.84	0.7467	3.4	2.08
11	0.7528	(i) 0.3083 (ii) 0.3126	(i) 2.86 (ii) 2.90	2.88	0.7676	3.3	2.06
12	0.8189	(i) 0.3250 (ii) 0.3075	(i) 2.77 (ii) 2.62	2.70	0.8236	4.0	1.72

Table 3.5
Equilibrium Water Content of Aminated (R-3) PS-DVB Resins

Duration of Nitration (hr)	Dry Weight of Aminated Resins (g) (1)	Wet Weight of Aminated Resins (g) (2)	Oven Dried Weight (g) (3)	Vacuum Dried Weight (g) (4)	Weight after three months	Shell 1 Moisture		Shell 2 Moisture		Shell 3 Moisture	
						(2) - (3)		(3) - (4)		(4) - (1)	
						G	%	g	%	g	%
0	1.0931	1.1823	1.0889	-		0.0939	-	00.00	0.0	00.00	0.0
1	1.3639	2.2026	1.6466	1.6451	1.3637	0.665	40.76	0.0015	0.11	0.2812	20.62
2	1.2136	2.3097	1.3738	1.3717	1.2141	0.9359	77.11	0.0021	0.17	0.1581	13.03
3	1.5321	2.6440	1.9000	1.8894	1.5330	0.7440	48.56	0.0106	0.69	0.3537	23.32
4	1.6319	2.9073	2.1381	2.1319	1.6327	0.7692	47.13	0.0062	0.37	0.5000	30.64
5	1.1216	2.0583	1.5785	1.5167	1.1228	0.4798	42.78	0.0618	5.5	0.3951	35.23
6	1.1138	2.2505	1.6305	1.6107	1.1151	0.6200	55.66	0.0198	1.77	0.4969	44.61
7	1.3124	2.3714	2.0094	2.0092	1.3135	0.3620	27.58	0.0002	0.02	0.6968	53.09
8	1.3376	2.1578	1.7183	1.7074	1.3381	0.4395	32.85	0.0109	0.82	0.3698	27.65
9	1.4924	2.8551	2.1537	2.1329	1.4929	0.7014	46.99	0.0208	0.014	0.6405	42.92
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

- Dry weight of the sample were taken after six months storage on December 1998. (The sample were placed in the dessicators on Jul 1998)
- Percentage calculation has been determined on the basis of dry weight given in column I.

Table 3.6
Equilibrium Water Content of TMA Modified (R-8) PS-DVB Resins

Duration of Nitration (hr)	Dry Weight of Aminated Resins (g) (1)	Wet Weight of Aminated Resins (g) (2)	Oven Dried Weight (g) (3)	Vacuum Dried Weight (g) (4)	Weight after three months	Shell 1 Moisture		Shell 2 Moisture		Shell 3 Moisture	
						(2) - (3)		(3) - (4)		(4) - (1)	
						g	%	g	%	g	%
0	1.0931	1.1823	1.0889	-		0.0939	-	00.00	0.0	00.00	0.0
1	1.3742	2.4632	1.6492	1.6402	1.3818	0.8140	59.23	0.0090	0.654	0.2660	19.36
2	1.2396	2.3129	1.5023	1.5020	1.2409	0.8106	65.39	0.0003	0.02	0.2624	21.17
3	1.3937	2.4937	1.7395	1.7241	1.3947	0.7542	54.11	0.0154	1.11	0.3304	23.71
4	1.4332	2.5719	1.8169	1.8144	1.4348	0.7550	52.68	0.0025	0.17	0.3812	26.70
5	1.5390	2.5987	2.0105	2.0053	1.5462	0.5882	38.22	0.0051	0.34	0.4663	30.30
6	1.1362	2.0371	1.5542	1.5385	1.1391	0.4829	42.50	0.0157	1.38	0.4023	35.41
7	1.7339	2.9189	2.4297	2.4164	1.7395	0.4892	28.21	0.0133	0.77	0.6825	39.36
8	1.4367	2.6168	2.0385	2.0345	1.4461	0.5793	40.32	0.0040	0.28	0.5978	41.61
9	1.4437	2.5127	2.0408	2.0239	1.4480	0.4719	32.69	0.0169	1.17	0.5802	40.19
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

- Dry weight of the sample were taken after six months storage on December 1998. (The sample were placed in the dessicators on Jul 1998)
- Percentage calculation has been determined on the basis of dry weight given in column I.

Table 3.7
Equilibrium Water Content of TEA Modified (R-9) PS-DVB Resins

Duration of Nitration (hr)	Dry Weight of Aminated Resins (g) (1)	Wet Weight of Aminated Resins (g) (2)	Oven Dried Weight (g) (3)	Vacuum Dried Weight (g) (4)	Weight after three months	(2) - (3)		(3) - (4)		(4) - (1)	
						G	%	g	%	g	%
0	1.0931	1.1823	1.0999	-	-	0.0934	8.5	00.00	0.0	00.00	0.0
1	1.5936	2.4579	1.8867	1.8806	1.7291	0.5712	35.84	0.0061	0.38	0.2870	18.01
2	1.7219	2.6108	2.0957	2.0666	1.1211	0.5151	29.91	0.0291	1.69	0.3447	20.02
3	1.1139	1.8163	1.3998	1.3825	1.1211	0.4165	37.39	0.0173	1.55	0.2686	24.11
4	1.2736	2.0059	1.7343	1.7248	1.2818	0.2716	21.33	0.0095	0.75	0.4512	35.43
5	1.1100	1.7048	1.5580	1.5450	1.1190	0.1468	13.23	0.0130	1.17	0.4350	39.19
6	1.4368	2.8789	2.0838	2.0772	1.4398	0.7951	55.34	0.0066	0.46	0.6404	44.61
7	1.4131	2.2137	2.0394	2.0344	1.4162	0.1743	12.33	0.0050	0.35	0.6213	43.97
8	1.3937	2.1176	1.9806	1.9731	1.3978	0.1370	9.83	0.0075	0.54	0.5794	41.57
9	1.4236	2.2381	2.0224	2.0177	1.4247	0.2157	15.15	0.0047	0.33	0.5941	41.73
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

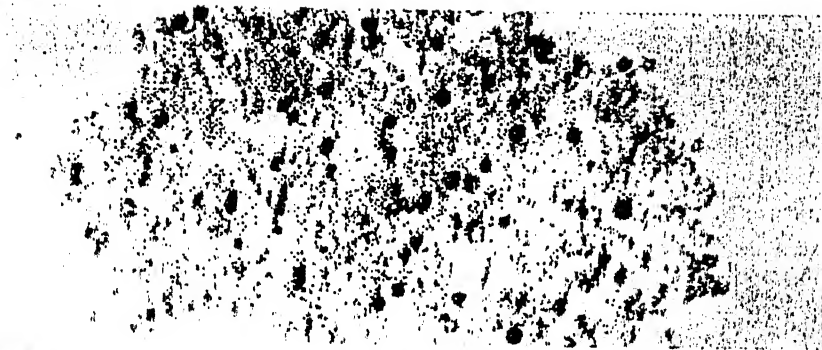
- Dry weight of the sample were taken after six months storage on December 1998. (The sample were placed in the dessicators on Jul 1998)
- Percentage calculation has been determined on the basis of dry weight given in column I.

Table 3.8
Equilibrium Water Content of TPP Modified (R-10) PS-DVB Resins

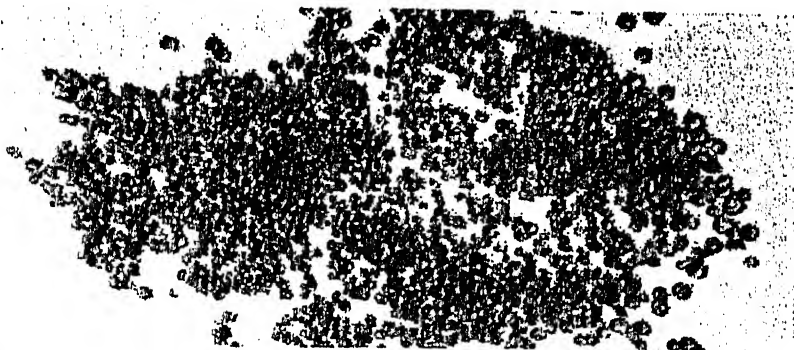
Duration of Nitration (hr)	Dry Weight of Aminated Resins (g) (1)	Wet Weight of Aminated Resins (g) (2)	Oven Dried Weight (g) (3)	Vacuum Dried Weight (g) (4)	Weight after three months	Shell 1 Moisture		Shell 2 Moisture		Shell 3 Moisture	
						(2) - (3)	(3) - (4)	(4) - (1)			
						g	%	g	%	g	%
0	1.0931	1.1823	1.0889	-	-	0.0939	8.59	00.00	0.0	00.00	0.0
1	1.7321	2.7786	2.1315	2.1158	1.7346	0.6471	37.36	0.0157	0.91	0.3837	22.15
2	1.5237	2.6600	2.0107	1.9992	1.5398	0.6493	42.61	0.0115	0.75	0.4755	31.21
3	1.6117	2.5601	2.2583	2.2422	1.6199	0.3018	18.73	0.0161	1.00	0.6305	39.12
4	1.1329	2.0832	1.5862	1.5709	1.1437	0.4970	43.87	0.0153	1.35	0.4572	40.36
5	1.4360	2.6718	2.1012	2.0924	1.4427	0.5706	39.74	0.0088	0.61	0.6564	45.71
6	1.4132	2.5531	2.0504	2.0466	1.4201	0.5027	35.57	0.0038	0.27	0.6334	44.82
7	1.1739	2.1817	1.7279	1.7256	1.1811	0.4538	38.66	0.0023	0.20	0.5517	47.00
8	1.2938	2.4701	1.8153	1.8108	1.2991	0.6548	50.61	0.0045	0.35	0.5170	39.96
9	1.3782	2.6391	2.0260	2.0148	1.3894	0.6131	44.49	0.0112	0.81	0.6366	46.19
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	47.36	0.004	0.04

- Dry weight of the sample were taken after six months storage on December 1998. (The sample were placed in the dessicators on Jul 1998)
- Percentage calculation has been determined on the basis of dry weight given in column I.

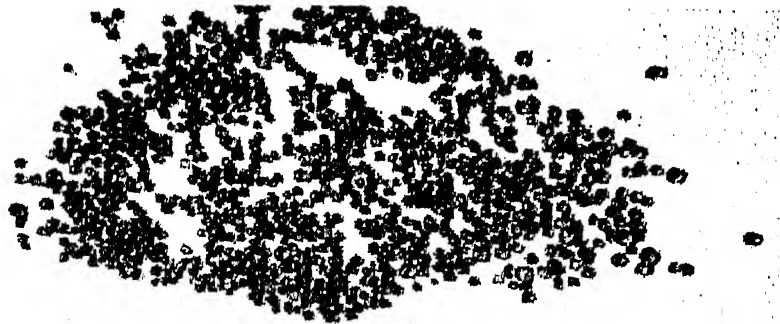
(a)



(b)



(c)



(d)

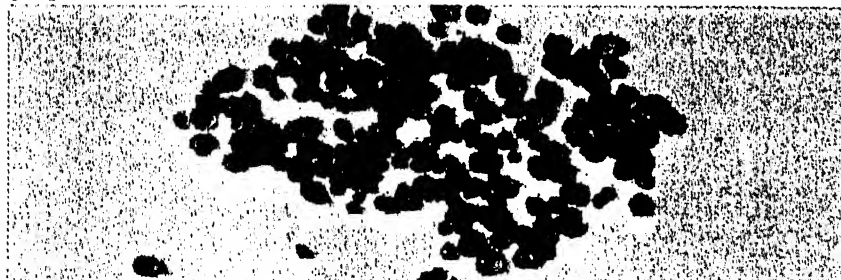


Figure 3.1 : Effect of modification on colour of PS-DVB resin

**(a) Unmodified, (b) Surface Nitrated, (c) Surface Aminated
(d) Epichlorohydrin reacted**

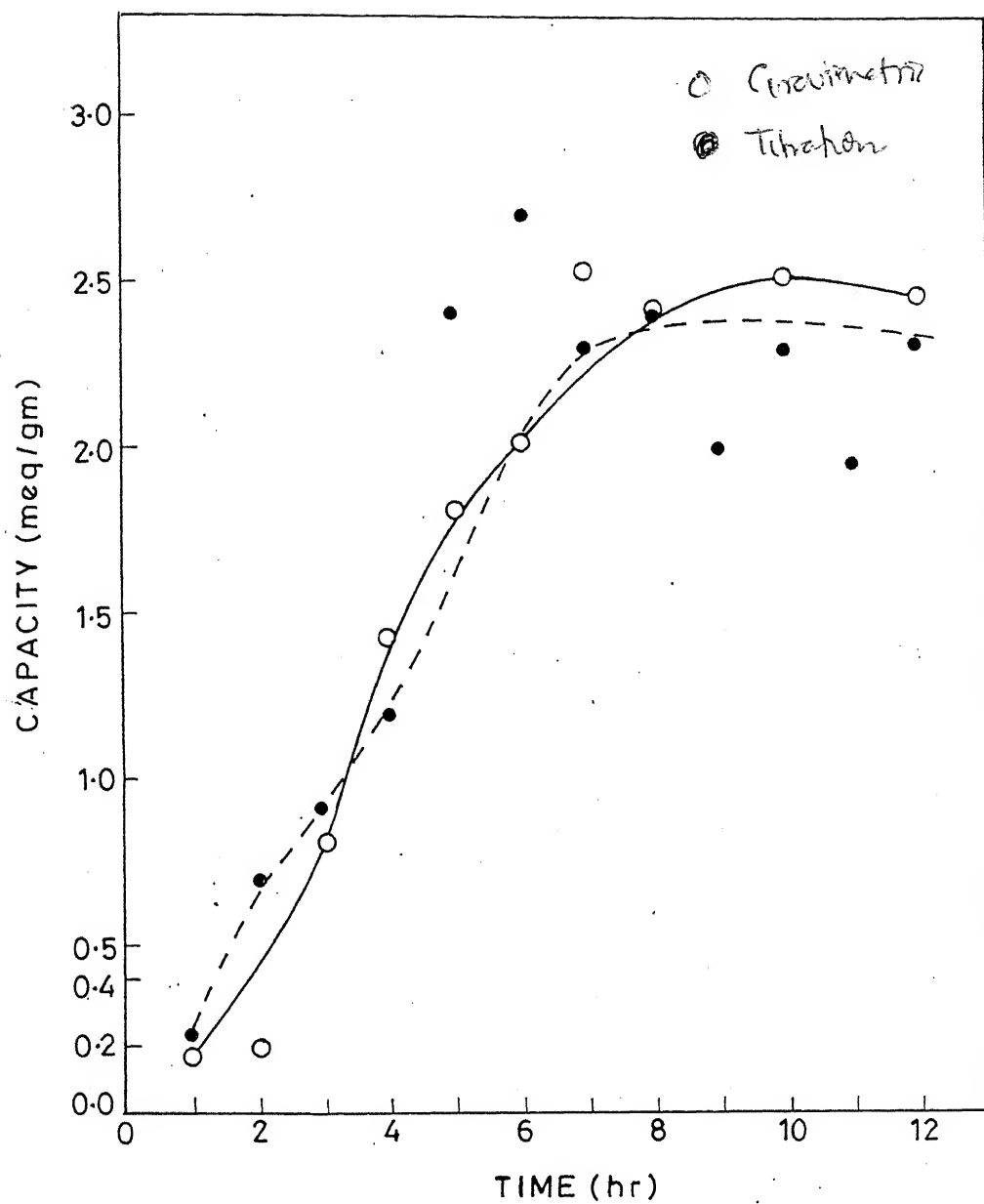


Figure 3.2: Effect of Nitration Time on the Capacity of Aminated PS-DVB Resin Modified by Epichlorohydrin

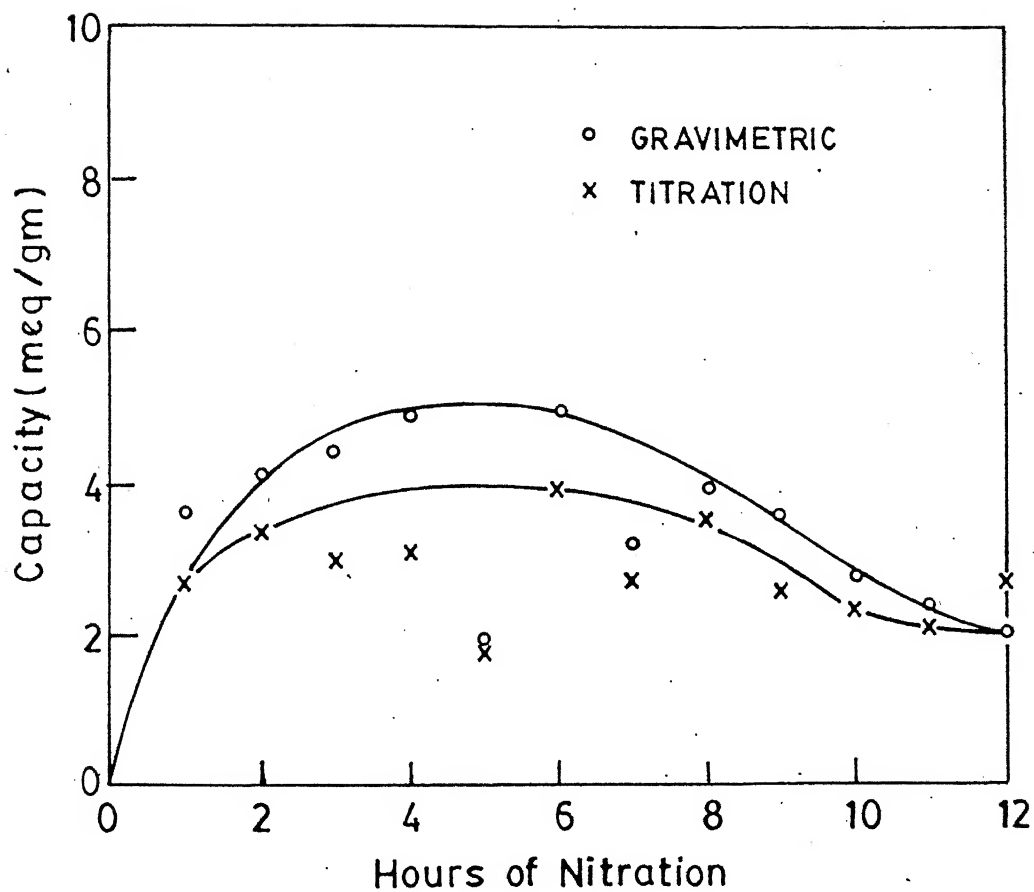


Figure 3.3: Effect of Nitration Time on the Capacity of PS-DVB Resin Modified by Trimethylamine

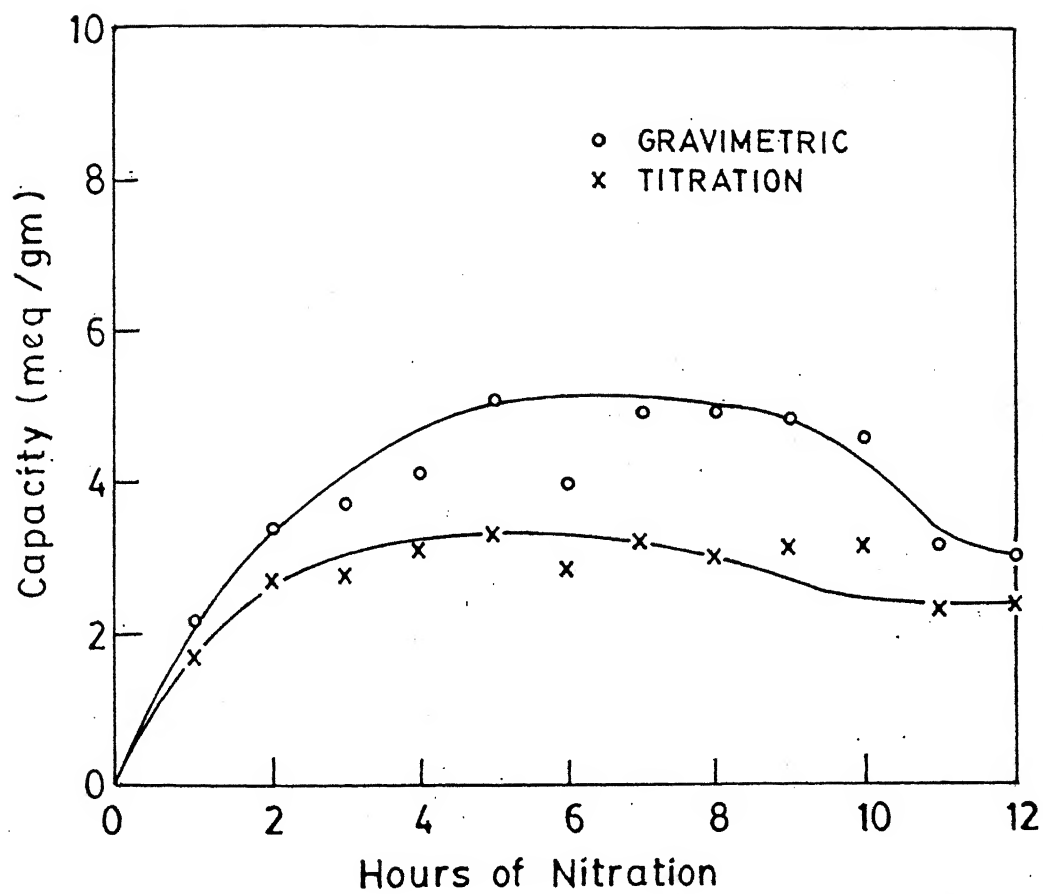


Figure 3.4: Effect of Nitration Time on the Capacity of PS-DVB Resin Modified by Triethylamine

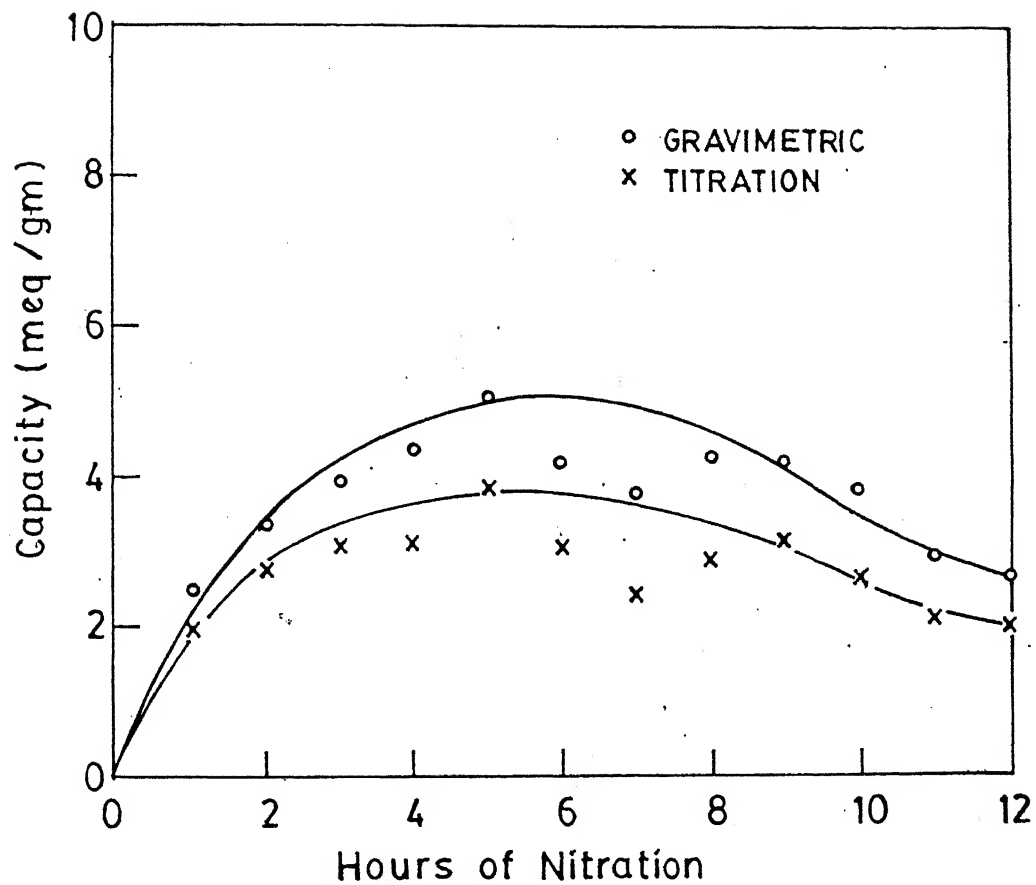


Figure 3.5: Effect of Nitration Time on the Capacity of PS-DVB Resin Modified by Triphenylphosphine

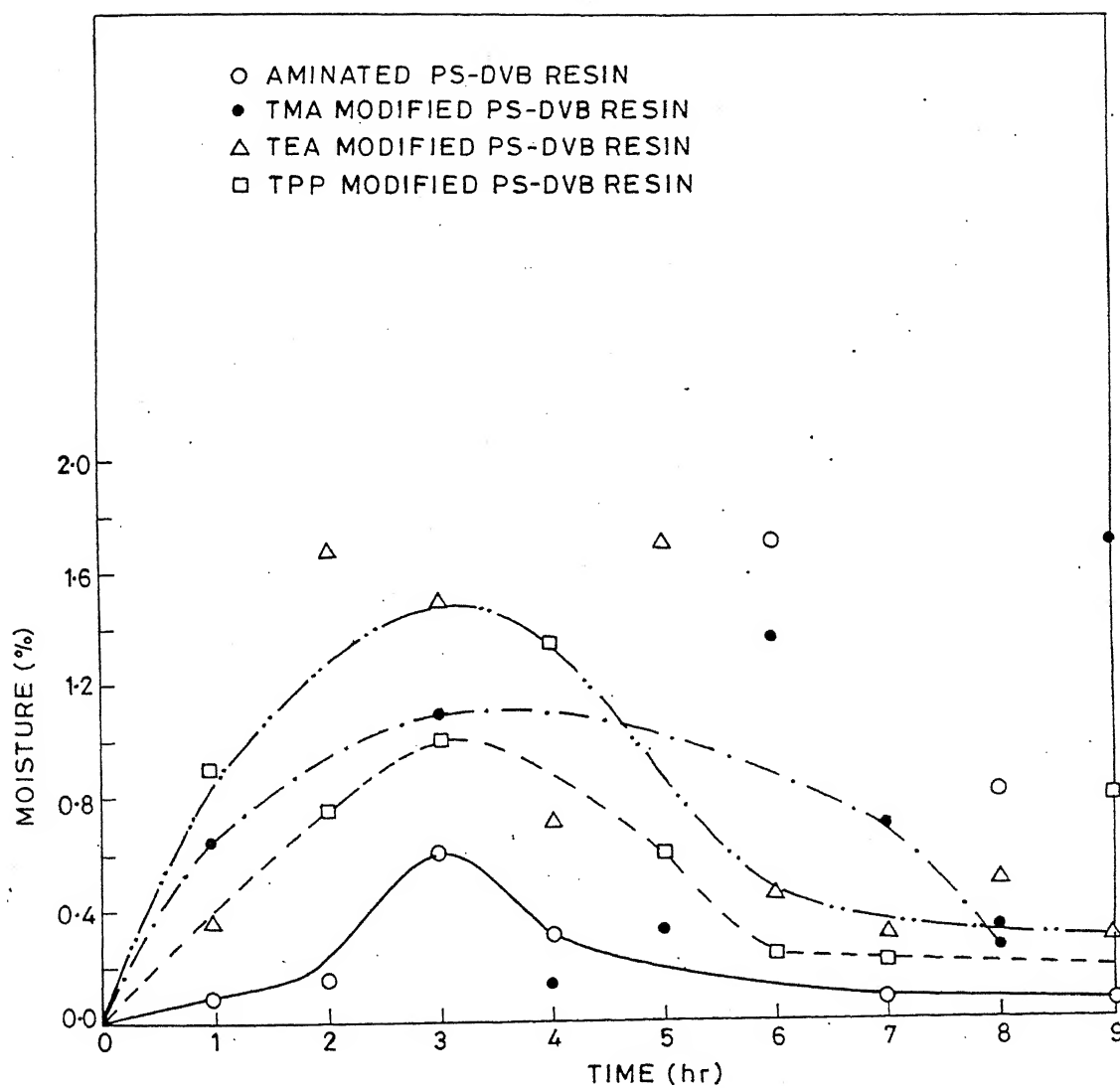


Figure 3.6: Shell 1 Moisture Content of Modified PS-DVB Resin

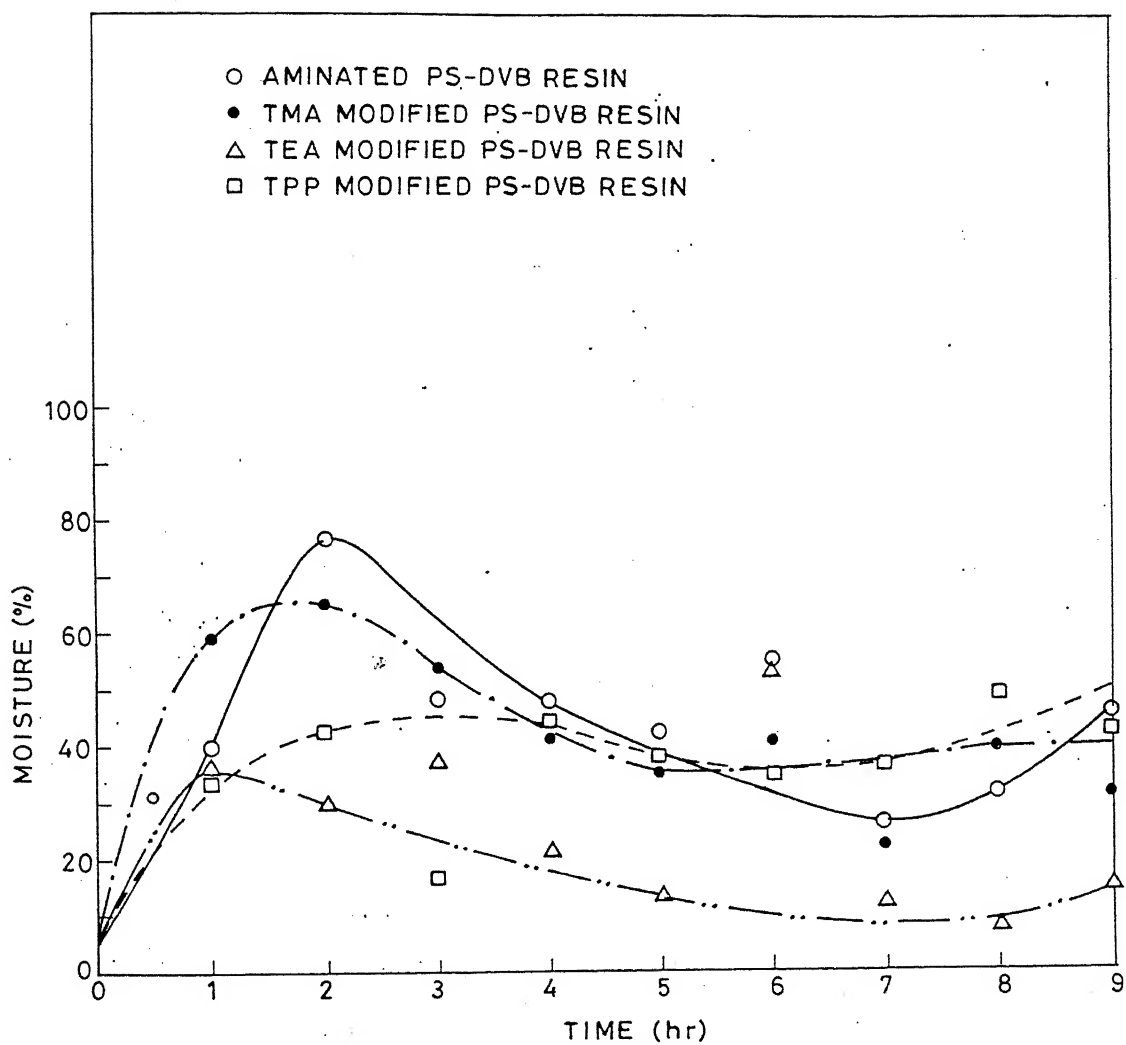


Figure 3.7: Shell 2 Moisture Content of Modified PS-DVB Resin

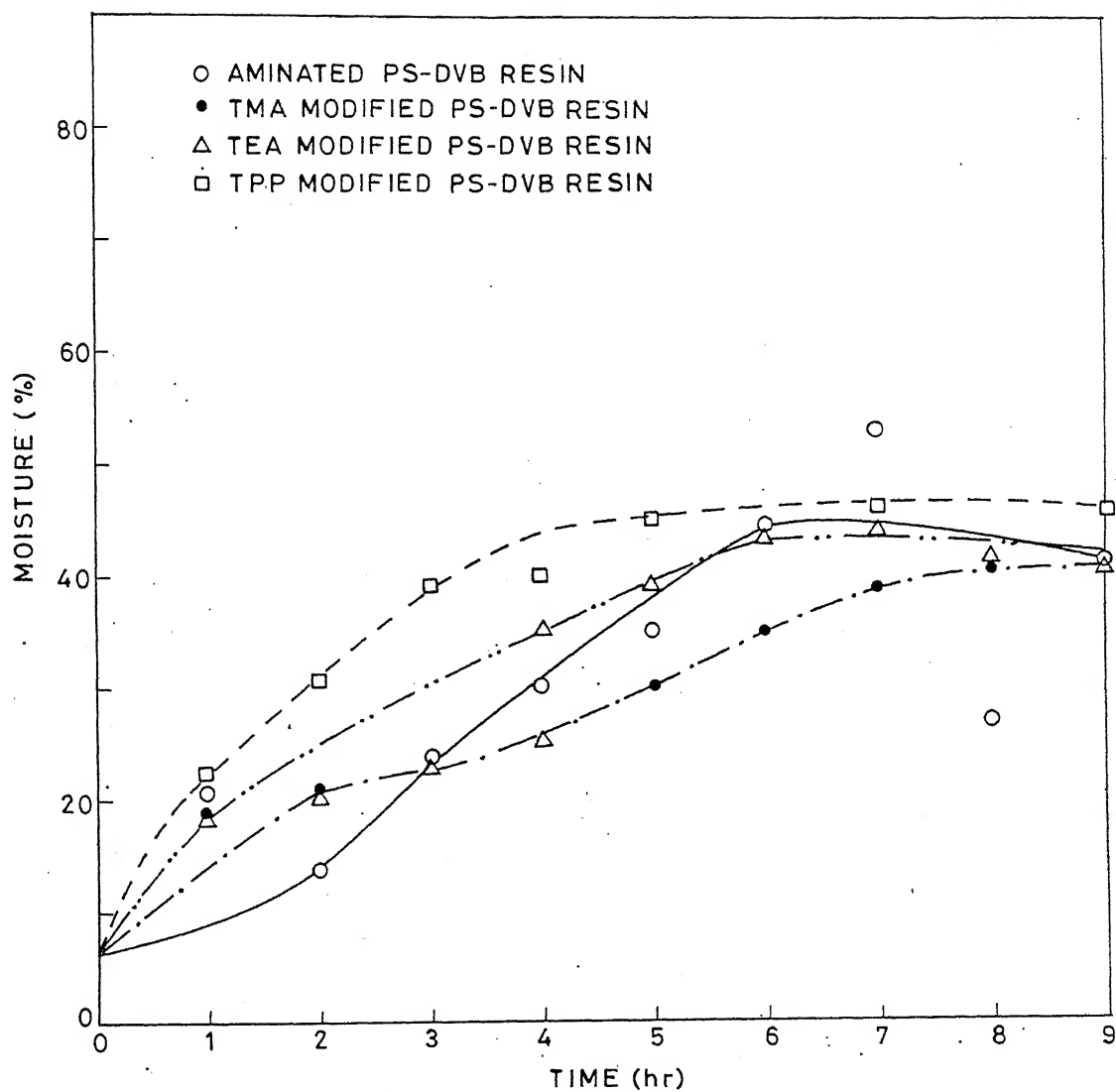


Figure 3.8 : Shell 3 Moisture Content of Modified PS-DVB Resin

Gas phase Nitration of PMMA-EDMA Resins

Introduction

The common polymeric material for anion exchange has been polystyrene-divinylbenzene copolymer and is highly hydrophobic due to phenyl rings. The other anion exchange materials have been made from polymers of acrylic and methacrylic acids by polymerization in presence of polyamines, crosslinked polyacrylonitrile which is hydrogenated using Raney nickel catalyst, reaction of this material with dihalocarbons, and amination of crosslinked polyvinyl chloroalkylether. Condensation polymers that have been used as anion exchange resins are obtained by polymerization of aromatic amine (such as phenylene diamine) with formaldehyde, polymerization of ethyleneimine and epichlorohydrin, condensation of urea with aldehydes, condensation of phenol, aldehyde and nitroparafins followed by reduction of nitro groups. All these materials have remained laboratory curiosity purely because these have poor mechanical strength and are not stable under repeated usage¹². The only commercial crosslinked polyacrylic (and copolymer of styrene acrylic acid) in use are cation exchangers which exchanges H^+ and used in stabilizing vitamin B₁₂ or as sustained release agents in drug formulation (See Table 1.2). In this thesis we report an extremely simple scheme of modification of crosslinked polymethyl methacrylate resin, which is stable under repeated use.

The macroporous methyl methacrylate crosslinked resin is completely aliphatic in nature and are more hydrophilic compared to PS-DVB copolymers. We have synthesized macroporous methyl methacrylate – ethylene glycol dimethacrylate (PMMA-EDMA) resin using similar suspension polymerization technique reported in Chapter 2. These have considerably higher mechanical strength, stable and are more

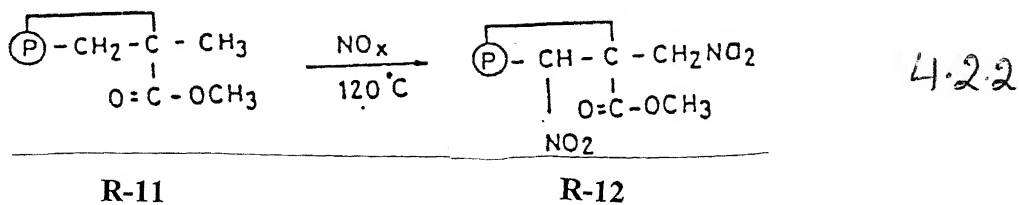
compatible with water medium. However they have never been used in the past as anion exchange resin purely because normal chemical modification schemes of chloromethylation do not work on PMMA-EDMA copolymer resin. The modification scheme using NO_x of chapter 2 is extremely effective and in the present study we show that the PMMA-EDMA resins are nitrated equally well.

4.2 Materials and Methods

4.2.1 Preparation of Macroporous Polymethylmethacrylate – Ethylene glycol Dimethacrylate (PMMA-EDMA) copolymer Resin

The crosslinked PMMA-EDMA resin is prepared by the process of suspension polymerization as discussed in section 2.2.1. We have prepared the macroporous resins in the size of 1mm by following the similar recipe as in the case of PS-DVB copolymer resin. In this case methylmethacrylate was used as monomer and ethylene dimethacrylate as the crosslinking agent. The recipe for the preparation of PMMA-EDMA resin consists of two phases. The organic phase has, methyl methacrylate (MMA) (280g, 2.8g-moles), Ethylene glycol dimethacrylate (EDMA) (80g, 0.41g-moles), azobisisobutyronitrile (AIBN) (4g, 0.025g-moles) and toluene (200ml, 2.18g-moles). As opposed to this, the aqueous phase consists of calcium carbonate (8g, 0.08 moles), Sodium sulfate (48g, 0.34g-moles), gelatin (0.031g) and distilled water (900 ml). These are mixed and under agitation polymerized for 4 h at 60°C and 3 h at 95°C. It was observed that particles start sticking and form a big lump when the gelatin content is reduced below 0.028 g similar to what was found in Chapter 2 for PS-DVB resins. To get polymer particles of the required size, this lump needed to be broken, which causes significant loss of material as well as energy. To overcome this difficulty we increased the gelatin content and it was found that 0.031 g of gelatin in the recipe is most appropriate in order to produce resins of the required size. The

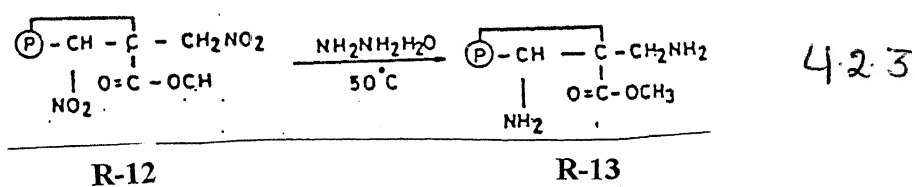
groups are more available for reaction, the nitration reaction on the PMMA-EDMA resins could be represented by



The methyl ester groups are known to be stable and are less likely to undergo modification. For this reason, the nitration of ($\text{O}=\text{C}-\text{OCH}_3$) has not been shown in eqn 4.2.2.

4.2.3 Amination of PMMA-EDMA Resins

To reduce the NO_2 functional group to amine groups within the PMMA-EDMA resin, it is heated with hydrazine hydrate at 50°C for four hours. The procedure followed is discussed in section 2.2.3. The colour of resin changes from pale yellow to golden yellow during the process of amination as shown in Figure 4.1. It is observed that the colour change is less prominent in the PMMA-EDMA as compared to the PS-DVB resin. Again the chemical changes take place only on surface and can be examined by the FTIR and ESCA.



4.3 Characterization of PMMA-EDMA Resin

Various chemical changes on the PMMA-EDMA resin has been characterized chemically as well as instrumently by standard techniques available to confirm the modifications. To carryout the characterization, we first performed elemental nitrogen detection test and the amount of NO_x consumed during the nitration.

4.3.1.1 Elemental Nitrogen Detection Test

The spot test for the nitrogen attached to PMMA-EDMA resin we have modified Lassaigne's test for detection of element nitrogen as discussed in section 2.2.5.

4.3.1.2 Estimation of NO_x Consumed During the Reaction

In order to estimate the NO_x consumed during the nitration reaction we determined the remaining NO_x after the nitration of each sample of the polymer resin. By subtracting the remaining NO_x with amount of NO_x fed we can estimate the actual amount of NO_x attach to the PMMA-EDMA resin. This procedure for evaluation of unconsumed NO_x is the same as that for the case of PS-DVB resins as discussed in section 2.3.2.

4.3.1.3 Determination of Capacity of PMMA-EDMA Resins:

In order to determine the exchange capacity of the PMMA-EDMA resin, we measured the capacity of these as per the procedures described by ASTM standards. (ASTM No. ASTM D 2187, 2687, 3087, 3375)¹¹⁰. The procedure followed for the determination of capacity is discussed in section 2.2.4. We determined the capacities by two methods, titrative as well as gravimetric methods and for a given method the average value reported in this work is average of two consecutive runs.

4.3.2 Instrumental Characterization

4.3.2.1 Fourier Transform for Infrared Spectroscopy (FTIR)

To examine the nitro group, we carried out the FTIR analysis of PMMA-EDMA resin and recorded the spectra for unmodified, nitrated and aminated PMMA-EDMA resin.

4.3.2.2 Electron Spectroscopy for Chemical Analysis (ESCA)

We carried out the ESCA of PMMA-EDMA resin, and determined the bond energies of C-N, C-O bonds. In this we analyzed the binding energies of individual carbon, oxygen and nitrogen and their shifting in modified PMMA-EDMA resins. The analysis is carried out for the blank nitrated and aminated PMMA-EDMA resin. The procedure of the technique is given in section 2.2.7.

4.3.2.3 Determination of Surface Area of PMMA-EDMA Resins :

Surface area plays a very vital role in any modification over the surface and it varies according to the modifications take place. To examine the effect of chemical modifications taking place in the PMMA-EDMA resin on the surface area, we have carried out the surface area analysis for the blank, nitrated and aminated samples of resin as per the procedure discussed in section 2.2.6.

4.4 Result and Discussion

4.4.1 Suspension Polymeriation of PMMA-EDMA Resins Formation

In this study crosslinked polymethyl methacrylate ethylene glycol dimethacrylate (PMMA-EDMA) resin in form of spherical particles have been prepared as per the recipe given in section 4.2.1. The prepared resin are macroporous in nature and in order to get the 1mm size particles we first used 0.028 g of gelatin as per the recipe used for PS-DVB. It was found that this amount of gelatin caused the formation of big lumps and the entire reaction mass became sticky in nature. In order to get the required size particles it is necessary to break this lump by hammer. This causes wastage of material and poor yield. To overcome this problem the amount of gelatin in the recipe has been increased. It is found that the 0.031 g of gelatin content is the optimum value to get the particle size of 1mm diameter.

4.4.2 Nitration of PMMA-EDMA Resin

Crosslinked PMMA-EDMA copolymer resin are sieved for getting the required sized resins of 1mm diameter and then subjected to nitration as per the procedure discussed in section 4.2.2. We took similar reaction conditions for nitration of PS-DVB resins for this and we first nitrated PMMA-EDMA resin at 130°C. It is found that this copolymer tends to degrade at this temperature but it does not at 120°C. Therefore we reduced the temperature of reaction and carried out nitration at 120°C. We carried out the nitration for 12 h having one hour step change and used the same reaction vessel as earlier. After nitration, resin is withdrawn from reaction vessel and it was found that the colour of resin changes from white to pale yellow as shown in Figure.4.1. The change in the colour indicates the extent of nitration of the PMMA-EDMA resin.

In order to determine the amount of NO_x consumed during the nitration step we followed the procedure given in section 4.3.1.2 and all experimental results are given in Table 4.1. The average values of the exchange capacity are plotted in Figure4.2. From this figure it is observed that on increasing the reaction time the formation of R-12 resin. This is checked by measuring consumption of NO_x as well as the exchange capacity of R-13 resin nitration increases slowly first and reaches on asymptotic value after 6 h of nitration. In order to confirm the nitration of the resin, we carried out the modified Lassaigne's test for detection of the elemental nitrogen as per the procedure of section 2.2.5. The prussian blue colour at the end of the test confirms the presence of nitrogen in the R-12 resin. To examine the nitration of the resin with NO_x we also carried out the FTIR spectroscopy of R-12 resin. A distinct peak in the region of 1200-1400 cm^{-1} shown in Figure 4.3 indicates the presence of NO_2 functional group over the surface of the PMMA-EDMA resin.

4.4.3 Amination of PMMA-EDMA Resin and Determination of Capacity

The nitrated PMMA-EDMA resin thus obtained are subjected to amination with the help of hydrazine hydrate. In the process of amination, the NO_2 group is reduced to amine group of R-13 resin according to eqn. 4.2.3. In order to examine the reduction of NO_2 group the FTIR spectra of R-13 is taken and it is found that the NO_2 peak of R-12 resin appear at 1350 cm^{-1} in the spectra which is completely eliminated in the spectra of aminated resin R-13 resin giving rise to amine group peak which appears 3500 cm^{-1} as shown in Figure 4.3.

In the next step we determined the exchange capacity of R-13 PMMA-EDMA resin according to the method of gravimetric estimation as discussed in section 4.3.1.3. The results are shown in Table 4.2 and are plotted in Figure 4.4. It is observed that the capacity of R-13 PMMA-EDMA resin increases as the nitration increases with time, followed by attainment of a broad maxima. After this there is a slight decrease in capacity for large times as opposed to aminated R-3 PS-DVB resin where the capacity attains an asymptotic value for larger times. This indicates that for large degree of nitration there is slight degradation of polymer which reduces its capacity.

4.4.4 Bond Energy Determination through ESCA

To carry out the elemental analysis of the nitrated R-12 PMMA-EDMA resin we determined the binding energy of different elements present on the surface of of this. For this purpose we carried out the ESCA analysis for our samples as described in section 2.2.7. We examined the blank(R-11), nitrated (R-12) and aminated (R-13) resins for survey scan in the range of 0-500 ev and 500-1000ev. From the information available from these survey scans each individual element (Oxygen O 1s, Nitrogen N

1s and Carbon C 1s) is scanned in its respective binding energy zone. We first scanned carbon in the range of 265-315 eV as shown in Figure 4.5. The standard sample gives C 1s peak at 284 eV. A distinct peak of C 1s for blank PMMA-EDMA resin is observed at 284.0. In nitrated resins C 1s peak appears at 285eV whereas in aminated resins the C 1s binding energy peak present at 284.2eV. The shifting in the peak portion of C 1s binding energy confirms the formation of C-N bonds. Figure 4.6 shows the individual scan of nitrogen in the range of 385-435eV for nitrated R-12 and aminated R-13 PMMA-EDMA resins. A characteristic peak of N 1s appears at 401.2 eV in the nitrated resins, which is in the nitrogen range of 395-410. This peak becomes more broad in the aminated resin and appear at 404.5eV which confirms the changes take place because of reduction of the NO_2 group to amine group. The N 1s peak position within the range of 395- 410ev confirms the formation of the C- NO_2 and C- NH_2 bond formation.

4.4.5 Effect of Temperature on Nitration of PMMA-EDMA Resin

As we have seen in Chapter 2, the nitration requires a high temperature. Here we have examined the effect of temperature on the nitration of PMMA-EDMA resin by varying the temperature at a step change of 10°C starting from 60°C upto 120°C . As we have reported earlier, the PMMA-EDMA particles tend to degrade beyond 130°C temperature, therefore we did not examine reaction temperatures more than this. The reaction time is set for twelve hours, after each set of experiments the NO_x consumption is determined and results are shown in Table 4.3 and Figure 4.7. The resin is then aminated with hydrazine hydrate and the capacity of the aminated resin is determined by gravimetric as well as titration techniques. The experimental results are given in Table 4.4 for two consecutive runs and the average value is plotted in Figure 4.8. We observed that as we increase the reaction temperature, the nitration

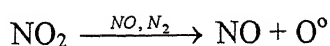
progresses to higher value. At lower temperatures, it does not produce any significant nitration and the nitration results are comparable at 110°C and 120°C.

4.4.6 Reproducibility of Experimental Data:

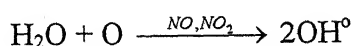
To check on reproducibility of experimental data, we have carried out the nitration of PMMA-EDMA resin thrice and the experimental results are given in Table 4.5. The capacity of aminated R-13 resin is given in the column 2 of this table. Some of this resin has been modified to R-18 according to the procedure given in Chapter 5 and their capacity were also determined and the results are given in Column 3 for each runs. In addition to this, the R-13 and R-18 resins after 6 (having capacity Q_{6h}) and 12 hrs (having capacity Q_{12h}) of nitration were subjected to seven regeneration cycles and the Q_{6h} and Q_{12h} recorded in the end of this table. The experimental results showed reproducibility of the same order as found for PS-DVB resins in Chapter 2.

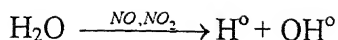
4.4.7 Determination of Rate Constant

In this study, we have modified the of PMMA-EDMA resin through gas phase nitration technique. We have shown that the NO_x intake by the resin during the nitration reaction increases asymptotically with time as we have seen in PS-DVB resin. We have described that the capacity of these nitrated resin increases with increasing temperature. Utilizing NO_x conversion and capacity data, we desire to determine the kinetics of reaction. We have shown in section 2.4.2 NO_2 produces NO and O radical in presence of atmospheric nitrogen¹¹⁴⁻¹¹⁵.

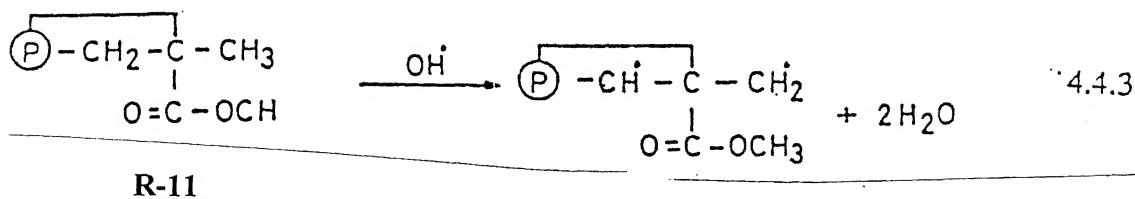


This oxygen radical thus formed reacts with moisture to give OH radical





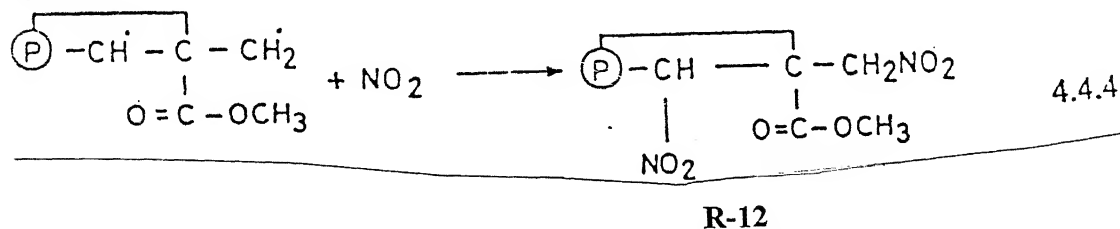
This active hydroxyl radical is assumed to abstract proton from the resin as follows



It may pointed out that the methyl ester above is stable and is less likely to react.

Since NO_2 has an unpaired electron, therefore it reacts readily with the radical sites as

follows



In order to determine rate constants, we first observe that the formation of nitrated R-12 resin is a multiple step process exactly as the formation of R-2 resin. In view of this, in order to analysis $[\text{NO}_x]$ versus t and Q versus t data for PMMA-EDMA R-11 resin, we once again assume 1st, 2nd and 3rd order kinetics and carry out the regression analysis. Results are given in Appendix A4.1 in which the regression line has been assumed to pass through the origin. Coefficient of correlation, r for $[\text{NO}_x]$ versus t data is similarly found to increase with increasing order of reaction while that for Q versus t data, it reduces as the reaction order is increased. Once again we can assume that the optimal results are obtained for the second order kinetics.

4.4.8 Effect of Modification on Morphology

In order to determine the changes taking place over the surface area of the PMMA-EDMA resin because of chemical modification, we recorded the SEM photographs at 1000, 1500 and 2000 magnifications and are shown in Figure 4.9 for

unmodified (R-11), nitrated (R-12) and aminated (R-13) resin after 6h of reaction. These photographs show a change in surface morphology after chemical modification. Small number of crests are present over the nitrated resin, which disappears after the aminated reaction. This confirms the changes take place in the surface morphology after the chemical modifications.

4.4.9 Effect of Modification on Internal Surface Area

We determined the internal surface area of PMMA-EDMA copolymer as per procedure discussed in section 2.3.6 and results are shown in Table 4.6. The unmodified resin has the internal surface area of $3.41 \text{ m}^2/\text{g}$, which is lower than that of unmodified PS-DVB resin. As the resin is modified, the surface area increases slightly but no definite pattern is observed. At higher duration of reaction it decreases, which is quite surprising. This may be because on modification the ability of the resin to retain moisture is increases as we observed in Chapter 3 and this retained moisture reduces the internal pores. However on seeing these data no further conclusion can be derived.

4.5 Conclusions:

It was observed that there are several types of anion exchange resins, which have been tested in laboratory but because of lack of mechanical strength and stability, they could not be commercially successful. Crosslinked polyacrylics which are in use in commercial application (recovery of vitamin B_{12} in Table 1.2) exchange H^+ and are cation exchangers. In this chapter, we have prepared anion exchange resin using macroporous PMMA-EDMA resin which is stable and has not been reported in literature.

We first prepared macroporous PMMA-EDMA resin by suspension polymerization. We subsequently nitrated this resin using NO_x at 120°C followed by

its reduction to amine group. The chemical spot testing, FTIR spectra and the ESCA analysis clearly confirm the formation of nitrate and amine bond formation within the resin. We have then determined the effect of duration of nitration upon the stability and the exchange capacity of the weak base resin. The capacity of common commercial anion exchange resin is 1meq/g while that of the material reported in this chapter is about 5meq/g.

Since the reduction of NO_2 gives NH_2 functional groups, the resin thus produced is a weak base. The experiments show that as the duration of nitration increases, the capacity of the resin increases and gives a broad maxima around 6 hours of nitration. For duration of nitration beyond this, the exchange capacity is seen to fall which is likely to occur because of degradation of resin. Since the PMMA-EDMA resin is mechanically very strong and is not affected by moisture or the nitration and amination reactions, this appears to be an ideal material for anion exchange resin.

Appendix A4.1

Linear Regression Analysis of Experimental Data of NO_x Consumption of Table 4.2 and Exchange Capacity of Resin of Table 4.3

As done in Appendix A2.1, we examine the 1st, 2nd and 3rd order kinetics and integrated form of the model equations are

(1) Gas Models:

Model 1

$$-\ln(1 - X_A) = k_1 t$$

Model 2

$$\frac{X_A}{1 - X_A} = C_{Ao} k_2 t$$

Model 3

$$\frac{2X_A - X_A^2}{(1 - X_A)^2} = 2k_3 C_{Ao}^2 t$$

Similarly, for the solid phase kinetic studies, the solid models have been taken as

(2) Solid Models:

Model 1

$$-\ln\left(1 - \frac{Q}{Q_\infty}\right) = k_1 t$$

Model 2

$$\frac{Q/Q_{\infty}}{1 - (Q/Q_{\infty})} = k_2 Q_{\infty} t$$

Model 3

$$\frac{Q/Q_{\infty} (2 - Q/Q_{\infty})}{(1 - Q/Q_{\infty})^2} = 2k_3 Q_{\infty}^2 t$$

where Q_{∞} is the asymptotic exchange (at $t = \infty$) capacity.

Since the consumption of NO_x as well as the capacity of modified resin both are zero at time $t=0$, the regression line chosen has to pass through origin and must have the following form.

$$y_{i,\text{model}} = ax_i \quad (\text{A4.1.1})$$

The regression analysis has been carried out exactly as done in Appendix A2.1. In the nitration of PMMA-EDMA resin we find the rise in conversion is more gradual and the spread of data is less compared to that for PS-DVB resin of Chapter 2. As we increase the order of the kinetic (see results in Tables A4.1 to A4.3), the fit of the data improves as seen from coefficient of correlation, r values. However, (see results of Tables A4.4 to A4.6) the Q versus t data are described better by lower order kinetic models. Since all NO_x functional groups shows up as NO_2 in the resin, it is desired to describe both these processes by the same kinetic model. In view of this, a second order kinetic model is an optimal description of the nitration process.

Table 4.1

Volume of NO_x Consumed (in ml/1.5g) During the Nitration of PMMA-EDMA Resin

Duration of Nitration (hr)	Titre value (ml)	Normality of N_{HNO_3}	Unconsumed NO _x During the Nitration (ml)	Consumed NO _x During the Nitration (ml)
1	92.0	0.184	412.16	37.84
2	89.1	0.178	398.72	51.28
3	88.7	0.177	396.48	53.52
4	83.0	0.166	371.84	78.16
5	73.8	0.147	329.28	120.72
6	68.3	0.137	306.88	143.12
7	61.5	0.123	275.52	174.48
8	65.6	0.131	293.44	156.56
9	67.2	0.134	300.16	149.84
10	68.7	0.137	306.88	143.12
11	93.1	0.186	416.64	33.36
12	96.5	0.193	432.32	17.68

Normality of NaOH 0.01N

Amount of NO_x fed 450 ml (300 ml/g)

Table 4.2

Capacity of Aminated PMMA-EDMA Resin Determined by Gravimetric Estimation

Duration of Nitration	Amount of Resins (g)	Wt. of ppt. For two consecutive runs (g)	Capacity (meq/g)	Average Capacity (meq/g)
1	0.6000	(i) 0.1576 (ii) 0.1421	(i) 1.83 (ii) 1.65	1.74
2	1.0176	(i) 0.4333 (ii) 0.4264	(i) 2.97 (ii) 2.93	2.95
3	0.7500	(i) 0.3709 (ii) 0.3622	(i) 3.45 (ii) 3.37	3.41
4	0.7572	(i) 0.4046 (ii) 10.4191	(i) 3.73 (ii) 3.87	3.80
5	0.7001	(i) 0.3918 (ii) 0.4242	(i) 3.91 (ii) (4.24	4.08
6	0.7000	(i) 0.3972 (ii) 0.3647	(i) 3.97 (ii) 3.64	3.81
7	0.7666	(i) 0.3259 (ii) 0.3393	(i) 2.97 (ii) 3.09	3.03
8	0.7057	(i) 0.4917 (ii) 0.4829	(i) 4.87 (ii) 4.78	4.83
9	0.7152	(i) 0.3660 (ii) 0.3747	(i) 3.58 (ii) 3.66	3.62
10	0.7374	(i) 0.5176 (ii) 0.5081	(i) 4.90 (ii) 4.81	4.86
11	0.7500	(i) 0.4876 (ii) 0.4722	(i) 4.54 (ii) 4.40	4.47
12	0.7517	(i) 0.3560 (ii) 0.3674	(i) 3.31 (ii) 3.42	3.37

Table 4.3

Volume of NO_x Consumed (in ml/1.5g) during the Nitration of PMMA-EDMA Resin

Duration of Nitration (hr)	60°C				70°C			
	Titre Value (ml)	Normality of HNO ₃	Unconsumed NO _x (ml)	Consumed NO _x (ml)	Titre Value (ml)	Normality of HNO ₃	Unconsumed NO _x (ml)	Consumed NO _x (ml)
2	35.9	0.179	402.62	47.38	86.9	0.174	389.64	60.36
4	87.2	0.175	390.89	59.11	89.4	0.179	400.52	49.48
6	92.3	0.185	413.86	36.14	84.7	0.169	379.64	70.36
8	86.0	0.172	385.64	64.36	81.1	0.162	363.51	86.49
10	83.6	0.167	374.83	75.17	79.6	0.159	356.82	93.18
12	84.7	0.169	379.64	70.36	77.9	0.156	349.24	100.76

Table 4 3, (Continued)

Volume of NO_x Consumed (in ml/1.5g) during the Nitration of PMMA-EDMA Resin

Duration of Nitration (hr)	80°C					90°C				
	Titre Value (ml)	Normality of HNO ₃	Unconsumed NO _x (ml)	Consumed NO _x (ml)	Titre Value (ml)	Normality of HNO ₃	Unconsumed NO _x (ml)	Consumed NO _x (ml)	Titre Value (ml)	Normality of HNO ₃
2	85.30	0.171	382.52	67.48	83.6	0.167	374.61	75.39		
4	83.7	0.168	375.24	74.76	63.3	0.127	283.61	166.39		
6	81.4	0.163	364.69	85.31	60.9	0.122	274.86	177.14		
8	78.2	0.157	350.64	99.36	58.1	0.116	260.64	189.36		
10	72.2	0.144	323.6	126.40	56.4	0.113	252.89	197.11		
12	73.2	0.146	328.09	121.91	58.73	0.117	263.11	186.89		

Table 4.3 (Continued)

Volume of NO_x Consumed (in ml/1.5g) during the Nitration of PMMA-EDMA Resin

Duration of Nitration (hr)	100°C					110°C				
	Titre Value (ml)	Normality of HNO ₃	Unconsumed NO _x (ml)	Consumed NO _x (ml)	Titre Value (ml)	Normality of HNO ₃	Unconsumed NO _x (ml)	Consumed NO _x (ml)	Titre Value (ml)	Normality of HNO ₃
2	80.9	0.162	362.82	87.18	70.1	0.140	314.09	135.91		
4	62.4	0.125	279.62	170.38	65.4	0.131	293.01	156.99		
6	55.3	0.111	248.13	201.87	43.7	0.087	195.82	254.18		
8	51.2	0.102	229.58	220.42	52.0	0.104	233.00	217.00		
10	49.7	0.099	222.82	227.18	52.1	0.104	233.97	216.03		
12	53.4	0.107	239.24	210.76	41.4	0.083	185.83	264.17		

Table 4.4
Capacity of Aminated PMMA – EDMA Resin Determined by Gravimetric Estimation

Duration of Nitration (hr)	60°C				70°C			
	Amount of Resin (g)	Wt. of ppt for two consec. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of Resin (g)	Wt. of ppt for two consec. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)
2	0.4394	a. 0.0233 b. 0.0246	a. 0.37 b. 0.39	0.38	0.4669	a. 0.0288 b. 0.0369	a. 0.43 c. 0.55	0.49
4	0.5739	a. 0.0329 b. 0.0445	a. 0.40 b. 0.54	0.47	0.5235	a. 0.0300 b. 0.0210	a. 0.40 b. 0.28	0.34
6	0.5285	a. 0.0137 b. 0.0152	a. 0.18 b. 0.20	0.19	0.4616	a. 0.0530 b. 0.0411	a. 0.80 b. 0.62	0.71
8	0.6057	a. 0.0435 b. 0.0539	a. 0.50 b. 0.62	0.56	0.5432	a. 0.0655 b. 0.0702	a. 0.84 b. 0.90	0.87
10	0.5136	a. 0.0590 b. 0.0560	a. 0.80 b. 0.76	0.78	0.6488	a. 0.0931 b. 0.0763	a. 1.00 b. 0.82	0.91
12	0.5229	a. 0.0525 b. 0.0435	a. 0.70 b. 0.58	0.64	0.6211	a. 0.0963 b. 0.0802	a. 1.08 b. 0.90	0.99

Contd...

Table 4.4 (Contd.)
Capacity of Aminated PMMA – EDMA Resin Determined by Gravimetric Estimation

Duration of Nitration (hr)	80°C				90°C			
	Amount of Resin (g)	Wt. of ppt for two conse. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of Resin (g)	Wt. of ppt for two conse. runs (g)	Capacity (meq/g)	Average Capacity (meq/g)
2	0.5512	a. 0.0364 b. 0.0554	a. 0.46 b. 0.70	0.58	0.4915	a. 0.0571 b. 0.0501	a. 0.81 b. 0.71	0.76
4	0.5404	a. 0.0558 b. 0.0512	a. 0.72 b. 0.66	0.69	0.5294	a. 0.1147 b. 0.1102	a. 1.51 b. 1.45	1.48
6	0.6316	a. 0.0462 b. 0.1042	a. 0.51 b. 1.15	0.83	0.5905	a. 0.1602 b. 0.1398	a. 1.89 b. 1.65	1.77
8	0.6237	a. 0.0904 b. 0.0832	a. 1.01 b. 0.93	0.97	0.6258	a. 0.1922 b. 0.1491	a. 2.14 b. 1.66	1.90
10	0.6011	a. 0.1078 b. 0.0957	a. 1.25 b. 1.11	1.18	0.5580	a. 0.1690 b. 0.1449	a. 2.11 b. 1.81	1.96
12	0.5833	a. 0.1130 b. 0.0695	a. 1.35 b. 0.83	1.09	0.5419	a. 0.1726 b. 0.1135	a. 2.22 b. 1.46	1.84

Contd...

Table 4.5
Results on Reproducibility of Nitration of PNDMA-EDMA Resin at 120°C

Duration of Rxn.(hr)	Run 1			Run 2			Run 3		
	1	2	3	1	2	3	1	2	3
1	37.84	1.74	1.11	51.53	1.68	1.19	25.66	1.71	1.16
2	51.28	2.95	2.49	55.67	2.85	2.28	60.34	2.86	2/32
3	153.52	3.41	2.79	125.35	3.36	2.68	145.65	3.50	2.76
4	178.16	3.80	2.11	140.49	3.91	1.93	162.7	3.87	1.98
5	220.72	4.08	2.75	253.7	4.13	2.82	230.5	4.15	2.81
6	243.12	3.81	3.23	239.8	4.01	3.28	278.5	3.98	3.29
7	274.48	3.03	3.11	260.3	3.25	3.20	290.7	3.13	3.26
8	256.56	4.83	3.10	273.5	4.69	3.16	264.8	4.73	3.19
9	249.84	3.62	3.08	261.7	3.81	3.22	250.4	3.69	3.15
10	243.12	4.86	3.34	240.3	4.82	3.49	231.5	4.75	3.45
11	233.36	4.47	2.51	250.5	4.35	2.69	241.8	4.42	2.63
12	217.68	3.37	1.80	240.6	3.61	1.72	230.7	3.53	1.77

- 1 : ml of NO_x consumed at 130°C
 2 : exchange capacity of R-13 resin in meq/g of wet resin found at 120°C
 3 : Exchange capacity of R48 Resin obtained by modification of R-13 Resin by Trimethylamine in meq/g of wet resin formed at 120°C

Table 9.5 (continued)

Reproducibility of Capacity of R-13 and R-18 Resin formed from Run 1 after 6 and 12 hr of Nitration

Regeneration Cycle No.	1	2	3	4
1	3.25	1.73	3.97	3.31
2	3.21	1.86	3.64	3.42
3	3.28	1.78	3.72	3.38
4	3.30	1.75	3.88	3.36
5	3.24	1.82	3.92	3.45
6	3.25	1.80	3.84	3.41
7	3.29	1.76	3.95	3.44

1. Capacity of TMA modified R-18 resin formed in Run 1 after 6 hrs of nitration in meq/g of wet resin
2. Capacity of TMA modified R-18 resin formed in Run 1 after 12 hrs of nitration in meq/g of wet resin
3. Capacity of TMA modified R-13 resin formed in Run 1 after 6 hrs of nitration in meq/g of wet resin
4. Capacity of TMA modified R-13 resin formed in Run 1 after 12 hrs of nitration in meq/g of wet resin

Table 4.5

Effect of Modification Surface Area

Types of Resin	Surface Area (m ² /g)
Unmodified PMMA-EDMA	3.41
Aminated PMMA-EDMA (One hour)	4.89
Aminated PMMA-EDMA (Two hour)	3.67
Aminated PMMA-EDMA (Three hour)	5.11
Aminated PMMA-EDMA (Four hour)	6.38
Aminated PMMA-EDMA (Five hour)	6.31
Aminated PMMA-EDMA (Six hour)	6.46
Aminated PMMA-EDMA (Seven hour)	6.80
Aminated PMMA-EDMA (Eight hour)	5.99
Aminated PMMA-EDMA (Nine hour)	7.09
Aminated PMMA-EDMA (Ten hour)	6.92
Aminated PMMA-EDMA (Eleven hour)	6.42
Aminated PMMA-EDMA (Twelve hour)	5.11

Table 4.5

Effect of Modification Surface Area

Types of Resin	Surface Area (m ² /g)
Unmodified PMMA-EDMA	3.41
Aminated PMMA-EDMA (One hour)	4.89
Aminated PMMA-EDMA (Two hour)	3.67
Aminated PMMA-EDMA (Three hour)	5.11
Aminated PMMA-EDMA (Four hour)	6.38
Aminated PMMA-EDMA (Five hour)	6.31
Aminated PMMA-EDMA (Six hour)	6.46
Aminated PMMA-EDMA (Seven hour)	6.80
Aminated PMMA-EDMA (Eight hour)	5.99
Aminated PMMA-EDMA (Nine hour)	7.09
Aminated PMMA-EDMA (Ten hour)	6.92
Aminated PMMA-EDMA (Eleven hour)	6.42
Aminated PMMA-EDMA (Twelve hour)	5.11

Table A4.1
Regression Analysis of 1st Order kinetics of $[\text{NO}_x]$ versus t data for Nitration of PMMA-EDMA resin.

T°K	k_1	Sr	St	r	σ
333	0.015	0.010	0.018	0.666	0.029
343	0.020	0.008	0.032	0.850	0.025
353	0.025	0.012	0.049	0.867	0.030
363	0.046	0.069	0.174	0.776	0.079
373	0.052	0.075	0.227	0.818	0.084
383	0.057	0.103	0.269	0.7842	0.095
393	0.058	0.230	0.524	0.748	0.108

Z : $\text{Sr} > \text{St}$ means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_1 = 233.54 \exp \left(-\frac{3182.77}{T} \right)$$

Table A4.2
Regression Analysis of 2nd Order kinetics of [NO_x] versus t data for
Nitration of PMMA-EDMA resin.

T°K	K ₂	Sr	St	r	σ
333	2.274	0.011	0.022	0.688	0.031
343	3.109	0.009	0.040	0.875	0.025
353	3.953	0.013	0.066	0.895	0.032
363	7.832	0.096	0.279	0.809	0.090
373	9.162	0.108	0.395	0.852	0.097
383	10.332	0.168	0.519	0.822	0.113
393	10.420	0.418	0.990	0.759	0.143

Z Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_2 = 1.536 \times 10^{-5} \exp\left(-\frac{3686.9}{T}\right)$$

Table A4.3
Regression Analysis of 3rd Order kinetics of [NO_x] versus t data for
Nitration of PMMA-EDMA resin.

T°K	k ₃	Sr	St	r	σ
333	332.68	0.051	0.104	0.709	0.067
343	466.55	0.040	0.204	0.896	0.050
353	608.62	0.056	0.357	0.917	0.068
363	1338.10	0.554	1.846	0.836	0.210
373	1622.53	0.664	2.869	0.876	0.239
383	1895.86	1.265	4.304	0.840	0.281
393	1897.11	3.352	7.913	0.759133	0.397197

∵ Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_3 = 1.20 \times 10^{-8} \exp \left(-\frac{4249.5}{T} \right)$$

Table A4.4
Regression Analysis of 1st Order kinetics on Q Versus t data for the capacity of PNMA-EDMA resin.

T/C	k ₀₁	Sr	St	R	σ
60	0.141	0.618	2.002	0.831	0.243
70	0.239	0.412	4.870	0.956	0.205
80	0.215	0.066	3.978	0.991	0.058
90	0.310	2.140	9.210	0.876	0.450
100	0.218	0.146	4.248	0.982	0.098
110	0.299	0.991	7.916	0.935	0.335
120	0.240	15.263	18.160	0.394	0.742

Z : Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{01} = 3.613 \exp\left(-\frac{994.3}{T}\right)$$

Table A4.5
Regression Analysis of 2nd Order kinetics on Q versus t data for Capacity of PMMA-EDMA resin.

T°C	k _{Q2}	Sr	St	R	σ
60	0.413	3.239	14.330	0.879	0.480
70	0.877	23.765	104.009	0.878	1.562
80	0.912	18.795	99.683	0.900	1.488
90	0.979	361.569	733.929	0.712	5.669
100	0.252	7 885111	78.007	0.948	1.000
110	0.492	248.455	589.248	0.760	5.012
120	0.580	2.175 x 10 ⁴	2.292 x 10 ⁴	0.226	22.711

Z : Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{Q2} = 0.104 \exp\left(\frac{623.60}{T}\right)$$

Table 4.6

Regression of 3rd order kinetics on Q versus t data for the Capacity of PMMA-EDMA resin.

T°C	k _{Q3}	Sr	St	r	σ
60	1.508	184.106	6.482 x 10 ⁻²	0.846	4.045
70	4.958	7.008 x 10 ⁻³	1.858 x 10 ⁻⁴	0.789	27.753
80	3.241	8.778 x 10 ⁻³	2.225 x 10 ⁻⁴	0.778	32.415
90	6.121	6.34 x 10 ⁻⁵	8.66 x 10 ⁻⁵	0.516	238.350
100	0.434	2.686 x 10 ⁻³	1.140 x 10 ⁻³	0.874	16.819
110	1.736	3.463 x 10 ⁻⁵	5.907 x 10 ⁻⁵	0.643	193.149
120	8.173	6.067 x 10 ⁻⁸	6.3 x 10 ⁻⁸	0.192	3.836 x 10 ⁻³

Z : Sr > St means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{Q3} = 8.076 \times 10^{-6} \exp \left(-\frac{403.52}{T} \right)$$

Table 4.6

Regression of 3rd order kinetics on Q versus t data for the Capacity of PMMA-EDMA resin.

T°C	k _{Q3}	Sr	St	r	σ
60	1.508	184.106	6.482×10^2	0.846	4.045
70	4.958	7.008×10^1	1.858×10^4	0.789	27.753
80	3.241	8.778×10^1	2.225×10^4	0.778	32.415
90	6.121	6.34×10^5	8.66×10^5	0.516	238.350
100	0.434	2.686×10^4	1.140×10^4	0.874	16.819
110	1.736	3.463×10^5	5.907×10^5	0.643	193.149
120	8.173	6.067×10^8	6.3×10^8	0.192	3.836×10^4

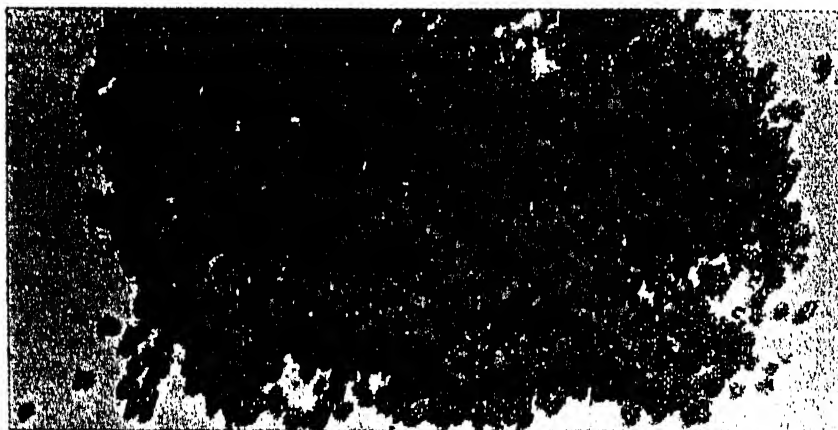
Z. $Sr > St$ means that $y = \bar{y}$ gives less total error compared to $y = ax$ line

$$k_{Q3} = 8.076 \times 10^{-6} \exp\left(-\frac{403.52}{T}\right)$$

(a)



(b)



(c)



Figure 4.2 : Effect of modification on colour of PMMA-EDMA resin

(a) Unmodified, (b) Surface Nitrated, (c) Surface Aminated

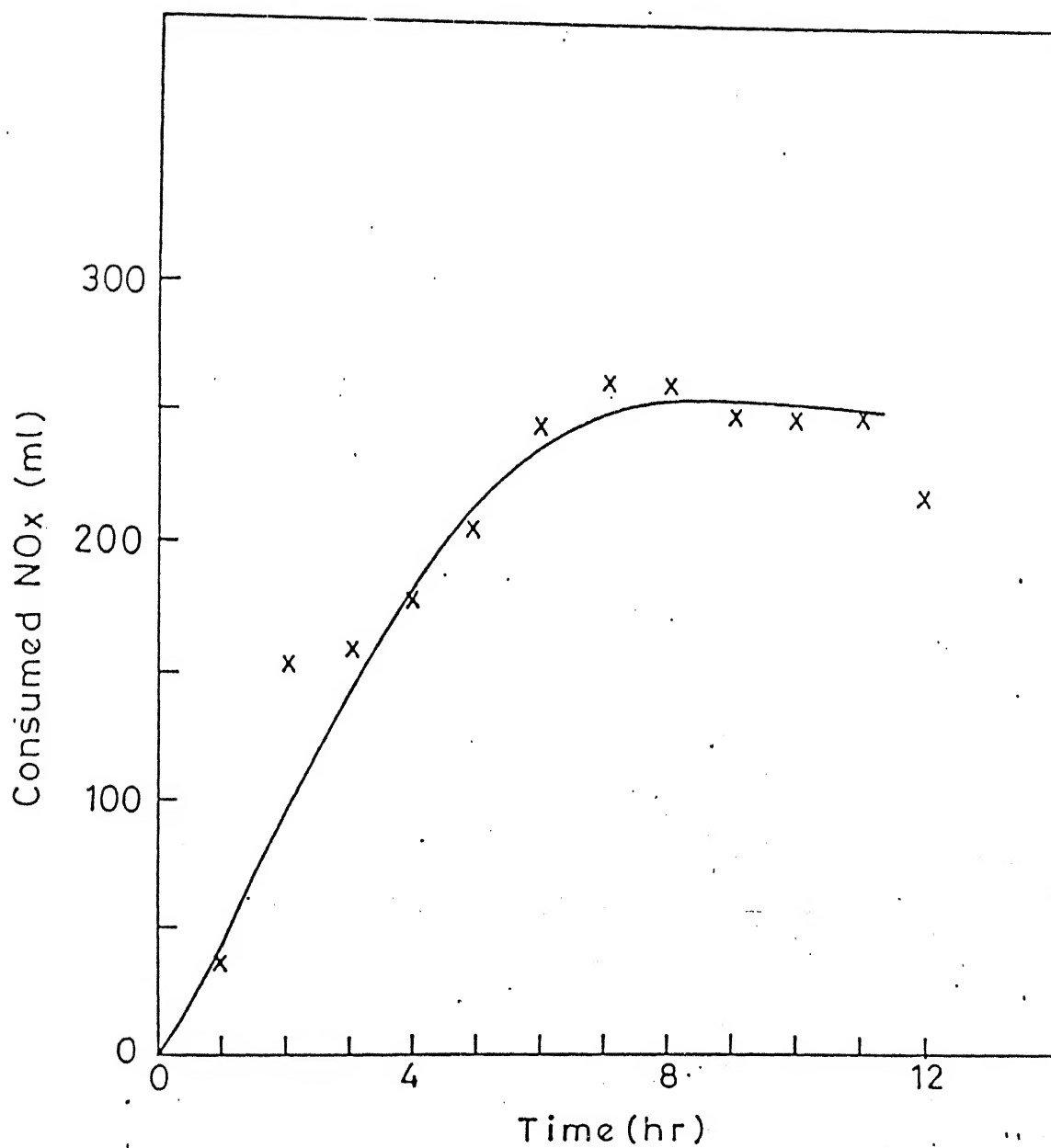


Figure 4.2: Amounts of NO_x Consumed During the Nitration of PMMA-EDMA Resin at 120 °C

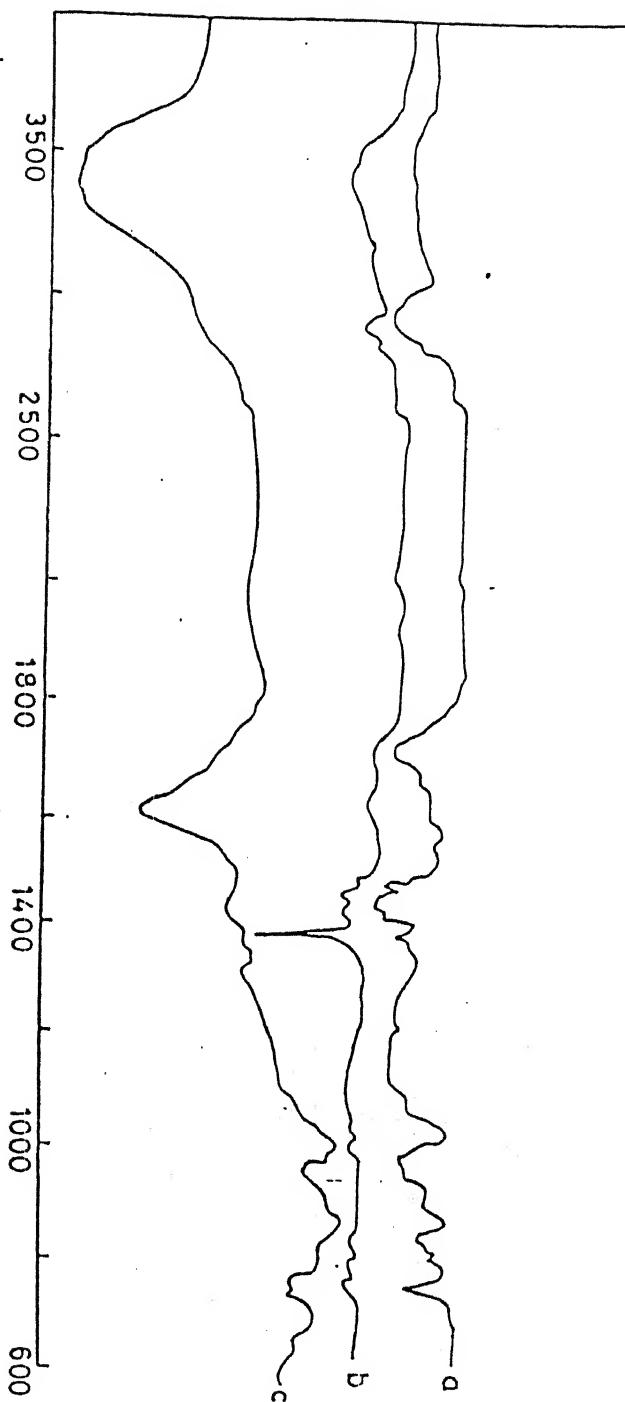


Figure 4.3: FTIR of (a) Unmodified, (b) Surface Nitrated and (c) Surface Aminated PMMA-EDMA Resin

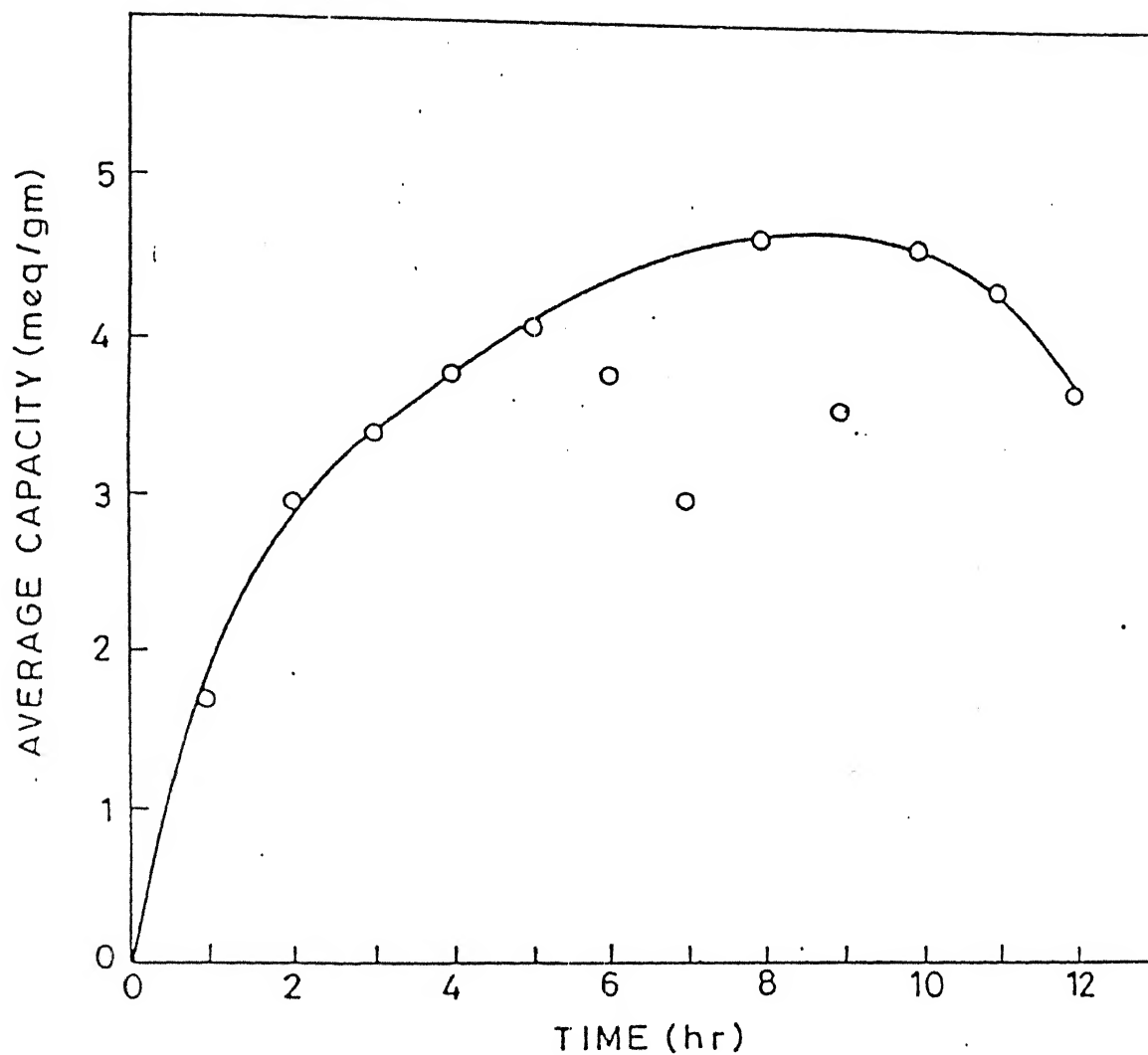


Figure 4.4: Effects of Nitration Time on the Capacity of Aminated PMMA-EDMA Resin at 120 °C

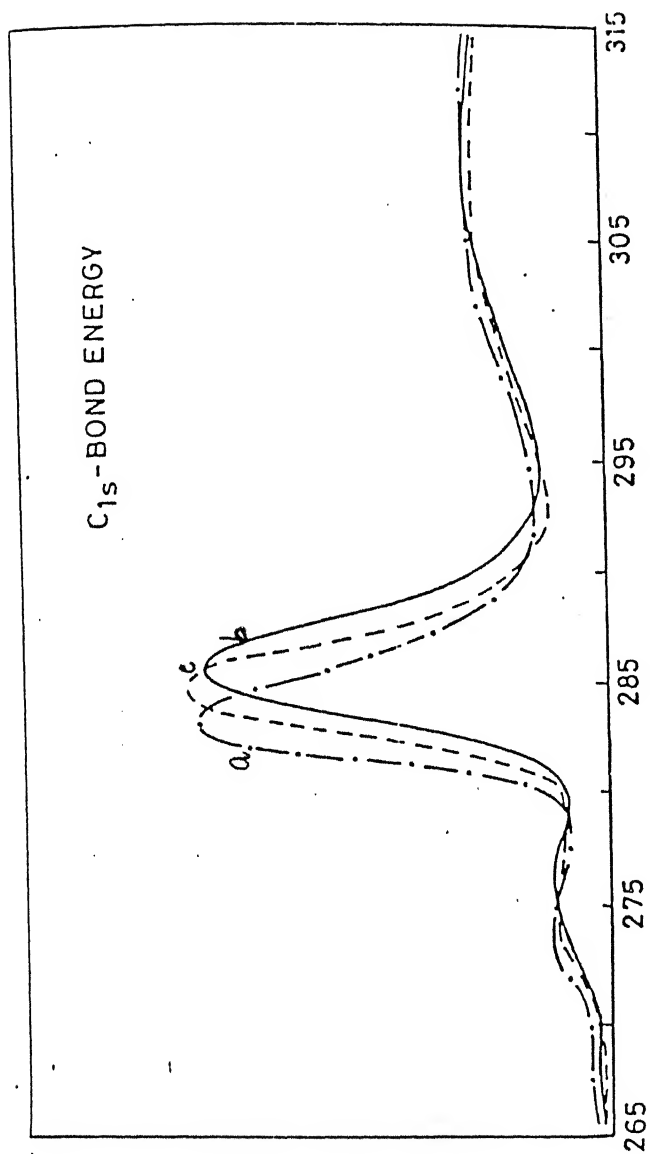


Figure 4.5: ESCA analysis for C_{1s} Bond Energy (a) Unmodified, (b) Surface Nitrate and (c) Surface Aminated PMMA-EDMA Resin

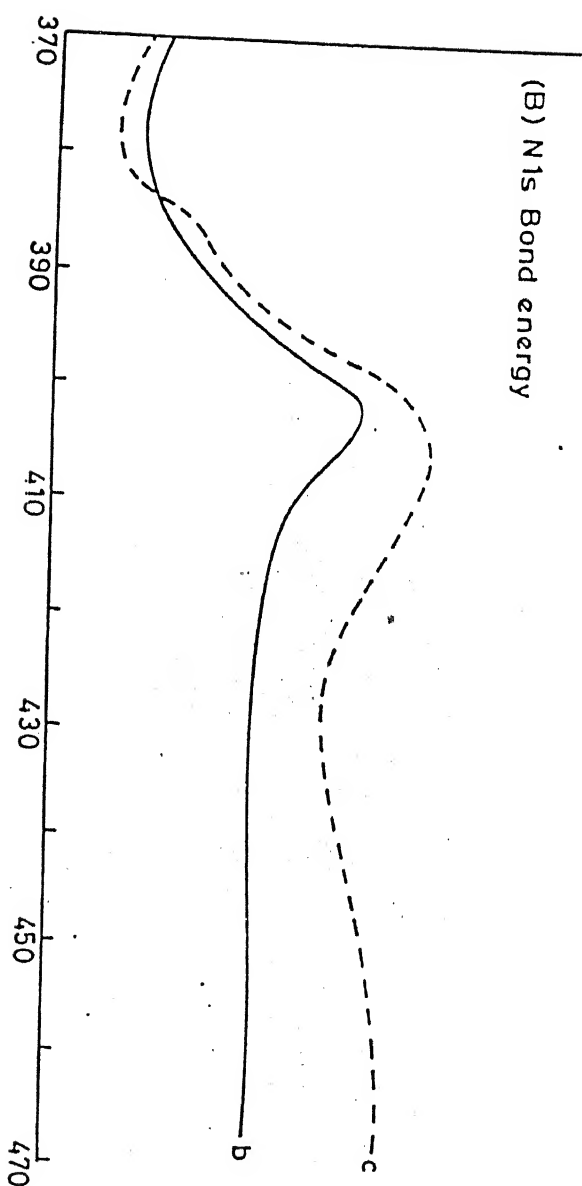


Figure 4.6: ESCA analysis for N_{1s} Bond Energy
(b) Surface
Nitrated and (c) Surface Aminated PMMA-EDMA Resin

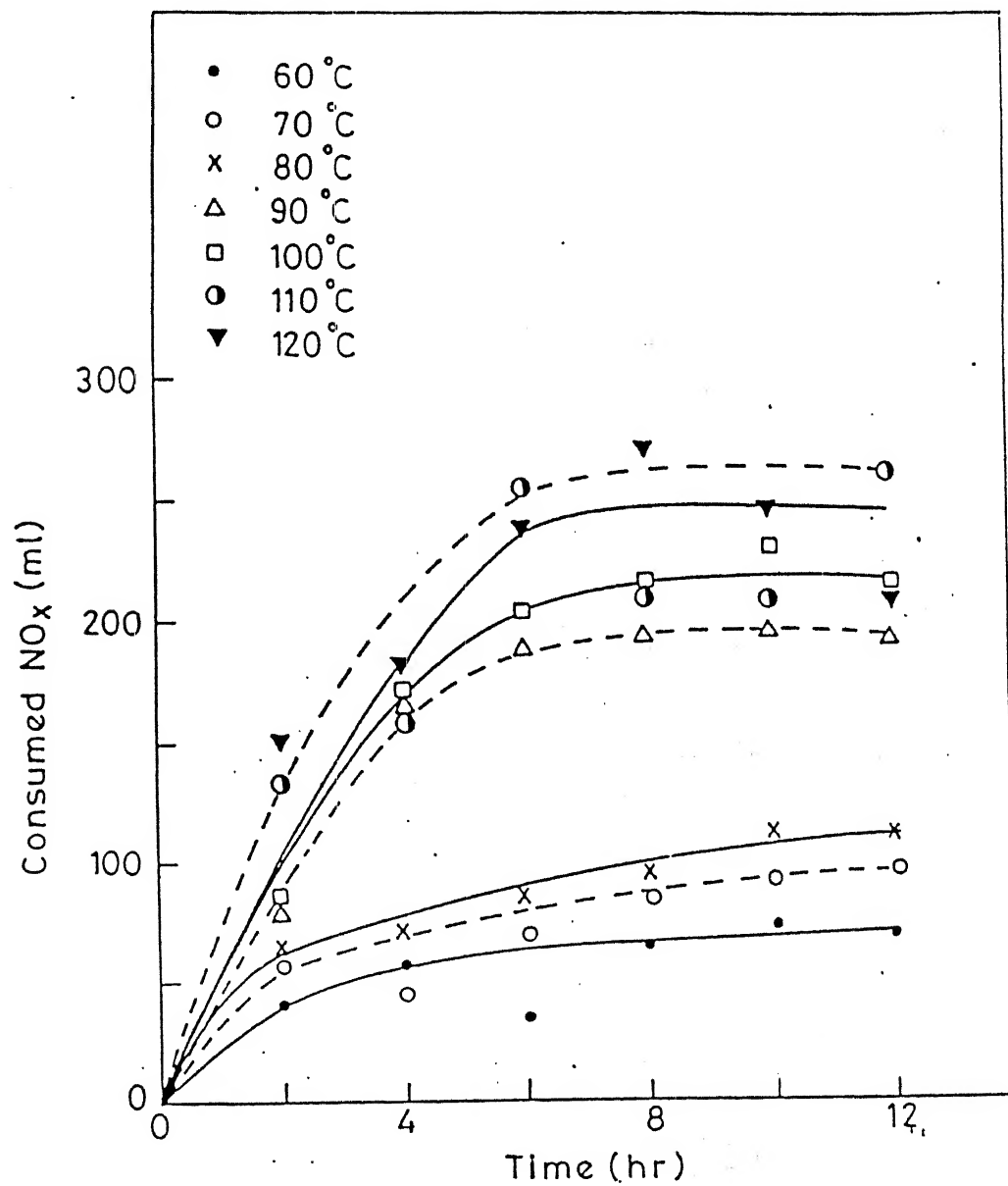


Figure 4.7: Effect of Time and Temperature on NO_x Consumption of PMMA-EDMA Resin

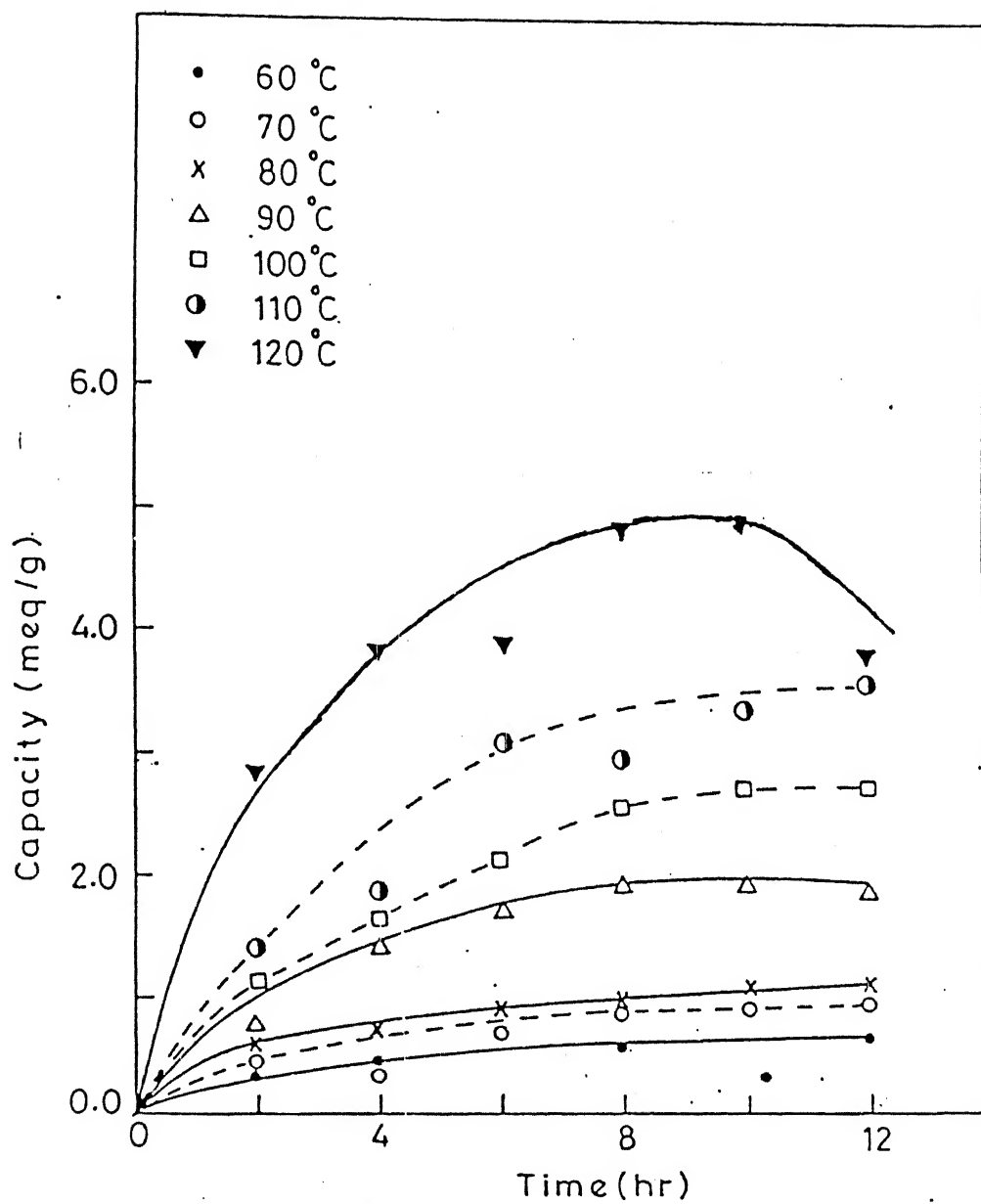
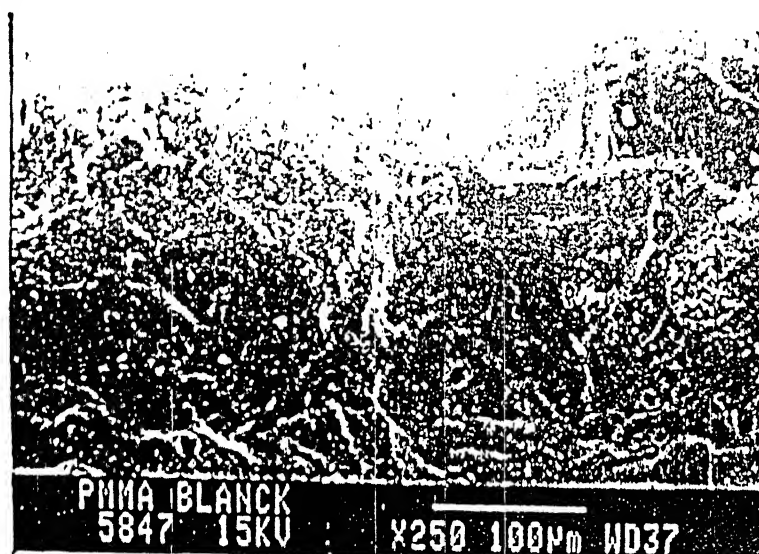
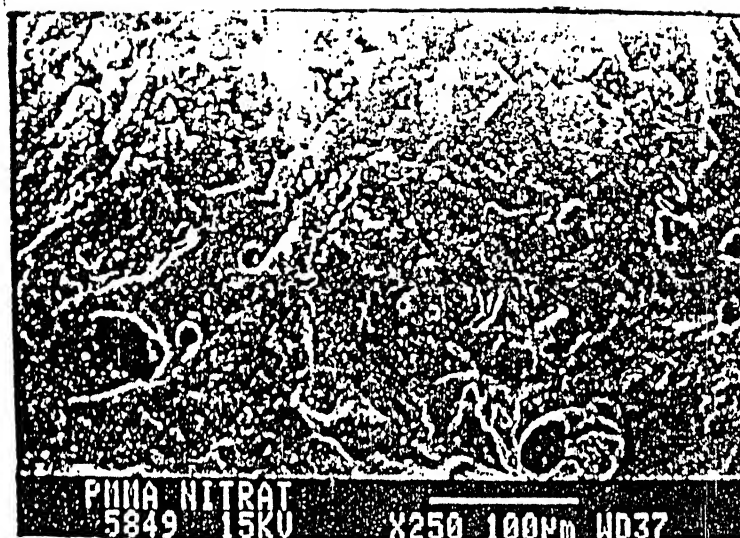


Figure 4.8: Effect of Time and Temperature on Capacity of PMMA-EDMA Resin

(a) Unmodified Resin



(b) Surface Nitrated Resin



(c) Surface Aminated Resin

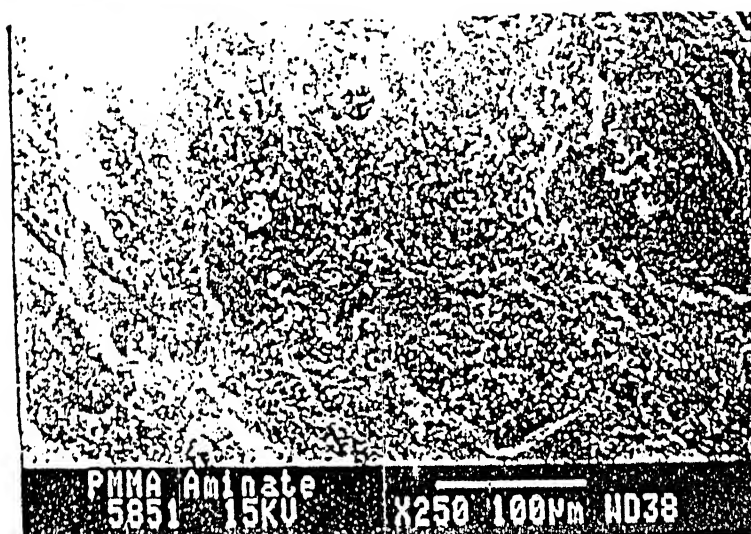


Figure 4.9 : Effect of surface modification on surface morphology of PMMA-EDMA Resin

Effect of Chloroethylation of Aminated PMMA-EDMA Anion Exchange Resin

5.1 Introduction

In chapter 4, we observed that common commercial acrylic base resins are cation exchanger with exchange group as H^+ and anion exchange resin based upon PMMA-EDMA has not been reported, we have developed a simple nitration technique and based on literature search of Chapter 1, the modification techniques using NO_x is new and represents a clean technology. In Chapter 2, we prepared crosslinked polystyrene-divinyl benzene copolymer resin and developed an entirely new and efficient gas phase technique for nitration and subsequent amination of PS-DVB resin. We examined the exchanger ability of these aminated PS-DVB (R-3) resin as an anion exchanger. It was found that these resins exchanged ions only once and could not be regenerated because of low pK values of aniline moiety. As a result of this, in Chapter 3 we chloroethylated these resins chemically to get regeneration possible as per ASTM methods. Subsequent salt preparation with trimethylamine, triethylamine and triphenyl phosphine gives strong base anion exchange resin, which has five times enhanced capacity.

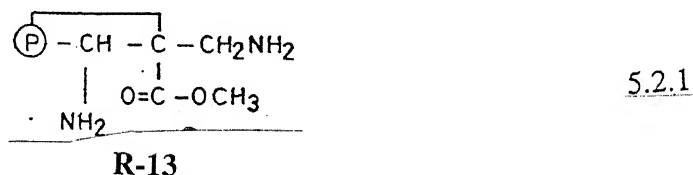
In Chapter 4 we prepared methacrylate PMMA-EDMA macroporous (R-11) resin which are completely aliphatic in nature and are expected to be more hydrophilic as compared to PS-DVB copolymer resins. This PMMA-EDMA resins were prepared using suspension polymerization technique and the basic advantage associated with these resin is that they have considerably higher mechanical strength, stable and more compatible with water. Our studies have shown that these resins are regenerable even without further modifications and has five times capacity of commercial resins. In this chapter, we have carried out chloroethylation of weak base

resin of Chapter 4 using epichlorohydrin and dichloroethane and determined capacity of these aminated weak and strong base macroporous PMMA-EDMA copolymer resins. We have examine the effect of time of nitration and various counter ions for these resin and compared the resin with PS-DVB resins prepared in Chapter 3.

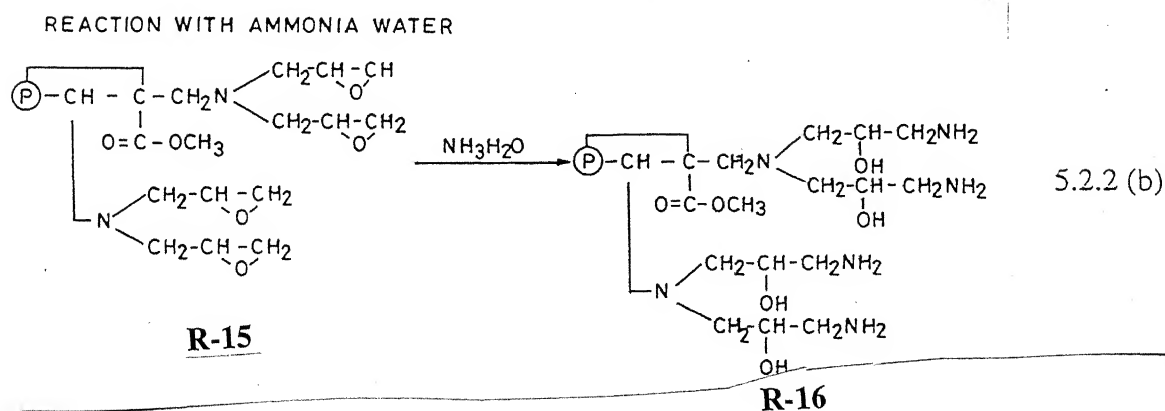
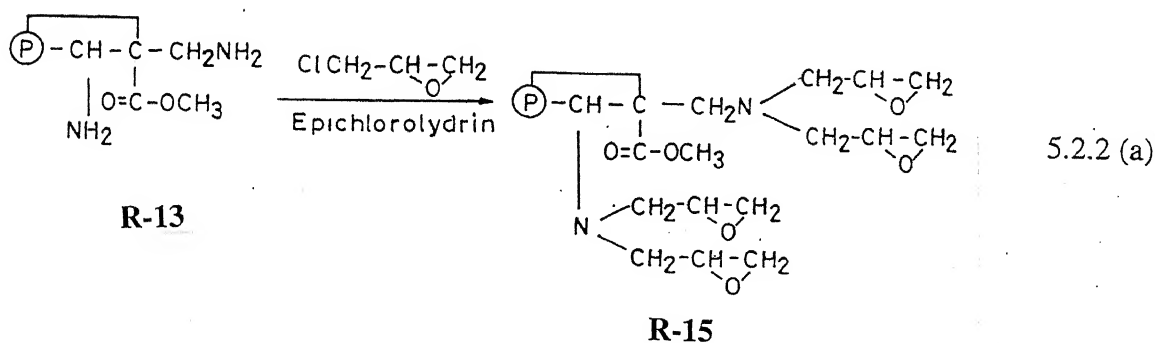
5.2 Experimental Procedure

5.2.1 Modification of Aminated PMMA-EDMA (R-13) Resins with Epichlorohydrin

The aminated PMMA-EDMA (R-13) resins were obtained using the nitration and amination procedure of Chapter 4. The resin thus obtained were further reacted with epichlorohydrin for four hours. The resin are refluxed with 50 ml of 5% v/v epichlorohydrin in ethanol (Section 3.1.3). Significant changes in colour were observed due to the modification and its photograph is shown in Figure 5.1. One repeat unit of the modified PMMA-EDMA resin can be shown as

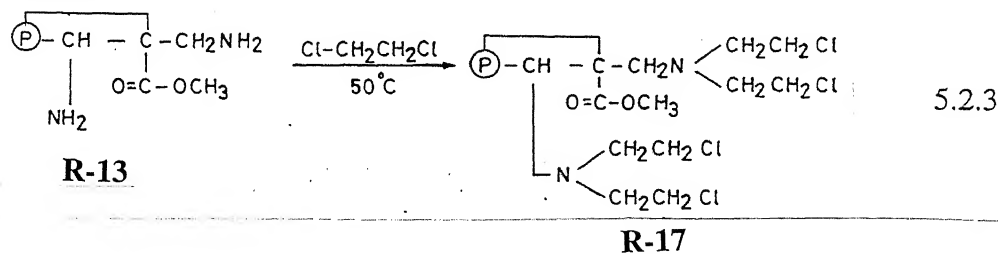


and the reacting modified resin with dichloroethane and further by epichlorohydrin can be represented by



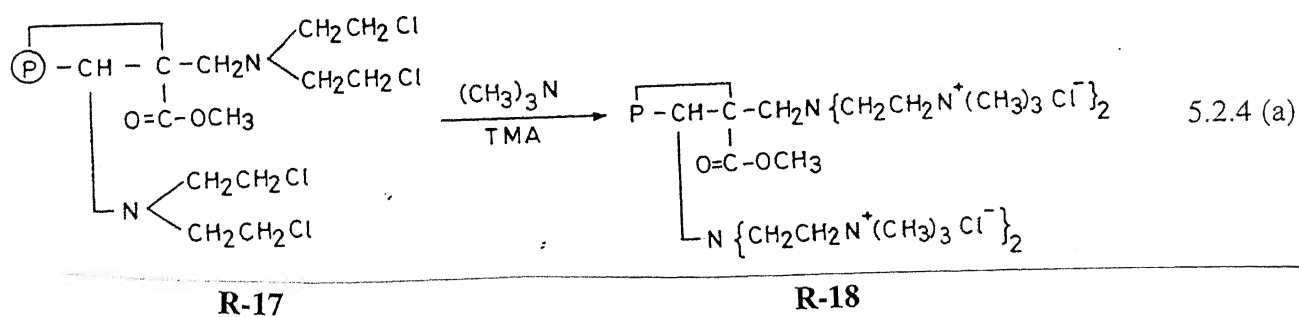
5.2.2 Preparation of Chloroethylated Strong Base PMMA-EDMA Anion Exchange Resin with Counter ions of trimethylamine, Triethylamine and Triphenylphosphine:

In order to form strong base anion exchange resin with trimethylamine, triethylamine and triphenyl phosphine as counter ion, the PMMA-EDMA (R-13) resins of Eqn.5.2.1 are reacted with dichloroethane first. Again higher concentration of dichloroethane is avoided in order to prevent the lump formation. The reaction occurred as follows

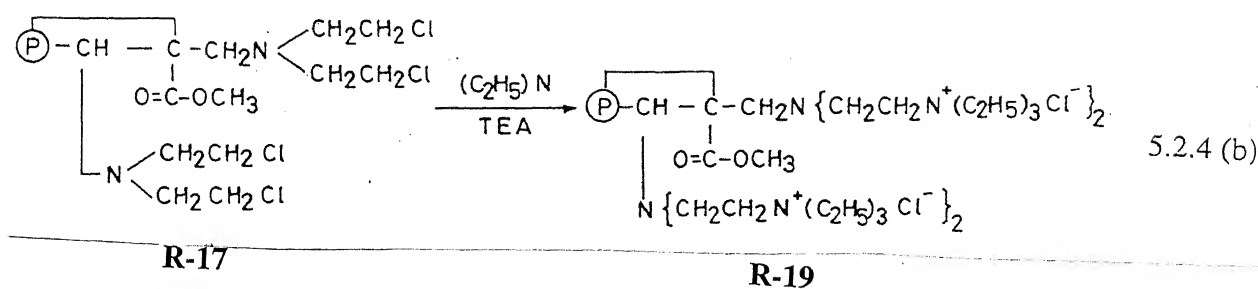


After modification with dichloroethane, the resin is dried and are further reacted with trimethylamine, triethylamine and triphenyl phosphine as per the method described in section 3.2.2. After completion of the reaction the resins are washed, dried and examined for the capacity and the moisture intake. The reaction occurring can be written as

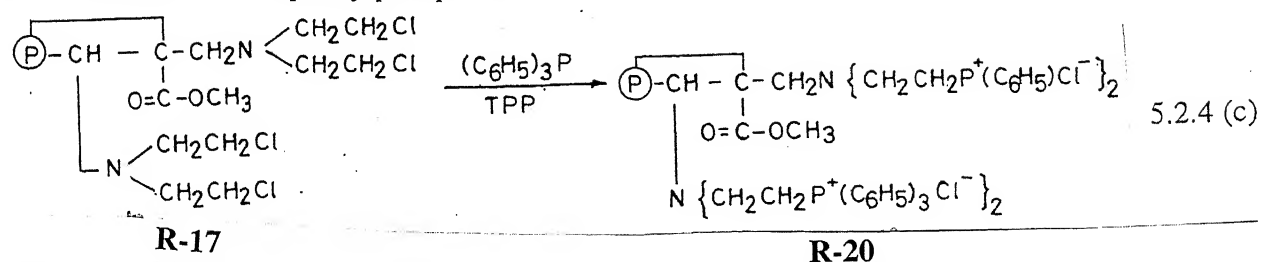
(i) Reaction with trimethylamine



(ii) Reaction with triethylamine



(iii) Reaction with triphenylphosphine:



5.3 Determination of Equilibrium Water Content

In order to determine the equilibrium water content, the strong base PMMA-EDMA resins, it is first saturated with moisture and then is subjected to oven and vacuum drying according to procedure discussed in section 3.3.

5.4 Result and Discussion

In Chapter 2 it was observed that the exchange capacity of the weak base aminated PS-DVB (R-3) resin goes down to zero during the second run and resins can not be regenerated by the ASTM¹¹⁰ procedure. In Chapter 3 we chloroethylated these aminated resins and the capacity of modified strong base PS-DVB resins improved having five times more than the commercial resin and could be regenerated like normal resin. In this chapter, we prepared PMMA-EDMA crosslinked copolymer (R-11) resin as reported in Chapter 4. The modification further improves the results and enhanced the capacity of PMMA-EDMA resins to about 4.8 as again 1 meq/g for

commercial anion exchange resin and can be explained on the basis of more nitration on the polymer matrix possibly occurring a CH_2 group on the back as the possible reaction site. Repeated runs have shown that the resins can be regenerated according to the ASTM procedure.

In order to examine the effect of further modification on its capacity, we reacted the aminated PMMA-EDMA copolymer (R-13) resins with Epichlorohydrin and dichloroethane. The reaction with the former gives a weak base resin and the amine group is separated from the resin by propyl moiety. As opposed to this, the reaction with dichloroethane amounts to chloroethylation of the polymer matrix. In order to determine the time effect, we nitrated the PMMA-EDMA resins systematically for twelve hours and samples of the resin taken out every hour. These hourly samples were aminated using hydrazine hydrate and then modified using epichlorohydrin as done earlier. We determined the extent of reaction of the resin by measuring its capacity as well as determining the unreacted NO_2 after varying the duration of nitration. Other parameters like time of amination, concentration of NO_x fed remained constant. It was observed that the duration of nitration played a very vital role in the final capacity of resin. We determined the capacity of these epichlorohydrin modified (R-16) resin, all experimental data are given in Table 5.1 and the average results on the capacity versus duration of nitration have been plotted in Figure 5.2. For each data point of Table 5.1 and this figure, the capacity were determined during two consecutive runs using both gravimetric and titration methods. It is observed that on increasing the duration of nitration, capacity first increases and after attaining a maximum value, there is a fall. The best results are obtained for 7 h of nitration with a maximum capacity of 2.9 meq/g, which is lower than 4.8 meq/g for aminated PMMA-EDMA resins. Evidently the modification is not efficient and per

amine site, no more than one epichlorohydrin is reacting along with the fact that several unreacted amines may have remained in the polymer matrix. It may be recalled that in Chapter 3, on increasing the duration of nitration, the number of functional groups increased and slight fall in capacity was explained on the basis of blocking of pores and consequent reduction in internal surface area.

We now compare the capacity results of PMMA-EDMA and PS-DVB resins after the modification with epichlorohydrin. On comparing figs. 5.1 and 3.1, we find that both are fairly similar in capacity. There is a slight increase in capacity of epichlorohydrin modified PMMA-EDMA (R-16) resins compared to epichlorohydrin modified PS-DVB (R-6) resin, the former having maximum capacity of 2.9 meq/g as opposed to PS-DVB, having 2.5 meq/g as its highest value. On comparing epichlorohydrin modified PMMA-EDMA (R-16) resins with aminated resins, we find that on modification with epichlorohydrin, the capacity value falls compared to directly aminated resin reported in Chapter 4. Epichlorohydrin is a large molecule and can give significant pore blockage, however propyl moiety separating the amine group from the resin may also play some role. This result is different compared to aminated PS-DVB (R-3) resins where the reaction with epichlorohydrin not only increases the capacity but makes it regenerable.

In addition to modification with epichlorohydrin, we have also examined the modification with dichloroethane and subsequently preparing their ammonium salts with trimethylamine (TMA), triethylamine (TEA) and triphenylphosphine (TPP). The exchange capacity of these strong base resins have been determined by the similar ASTM and BIS procedures¹¹⁰ and all experimental data are given in Tables 5.2 to 5.4. The plot of resin capacity versus duration of nitration in Figures 5.3 to 5.5 is the

average of two consecutive runs. Some of these resins were subjected to several exchange experiments in order to show that resin can be regenerated and can be used as an anion exchanger.

It is observed that there is a fast rise in capacity for short duration of nitration followed by the attainment of a broad maxima at around 7 hours of nitration. Slight fall in the capacity for large durations of reaction is observed. From these experimental results it is clear that the modification of PMMA-EDMA resins by dichloroethane resins does not produce any substantial change in the exchange capacity as it did for PS-DVB resins and increase in capacity is about 10% more than the aminated resin. This indicates that under the condition of reaction, only one dichloroethane molecule has reacted per amine site and after this reaction the secondary amine is not participating in the exchange reaction. This strong base resin has an exchange capacity of around 5 meq/g which is a considerably high compared to commercial anion exchange resins. No change in exchange capacity on further modification could likely be due to small change in solvation due to modification with dichloroethane. For small nitration the pores are likely to offer less resistance to the ion exchanging liquid and the exchange capacity increases. As the degree of nitration increases the blockage of pores occur which ultimately leads to a decrease in capacity.

In order to assess, the solvation ability, we have determined the equilibrium water content by the procedure discussed in section 3.4. The Shell 1, shell 2 and shell 3 moisture content have similarly been determined for strong base resins having TMA, TEA and TPP counter ions. All intermediate experimental data are given in Tables 5.5 – 5.8 and different shell moistures plotted in Figures 5.6 – 5.8. As seen in Table 5.5, the unmodified PMMA-EDMA (R-11) resin retains 9.35% as shell 1

moisture, which is higher than that of PS-DVB (R-1) resin which contains 8.59% as shell 1 moisture. In case of aminated resin the shell 1 moisture content first increases as the duration of nitration increases but it falls for larger time of nitration. This reduction in shell 1 moisture occurs with simultaneous fall in shell 2 moisture as seen in figures 5.7 and 5.8. The fall in shell 1 and shell 2 moisture is more prominent in aminated weak base PMMA-EDMA resins as compared to modified strong base resin (for all three counter ions) where the fall in moisture is very broad. However shell 3 moisture reaches an asymptotic value for larger time as opposed to aminated resins.

In the case of TEA and TPP modified PMMA-EDMA (R-19 & R-20) resins the shell 1 moisture and shell 3 moisture first increase as the duration of nitration increases and for larger duration it attains an asymptotic behaviour. For shell 1 moisture it follows the same trend as the unmodified aminated resins and it first increases to a maxima then a slight fall is observed. It is also observed that all the three states have less moisture content as compared to PS-DVB resins that we have reported in Chapter 3. This indicates that the modified PS-DVB resins are more hydrophilic compared to the modified PMMA-EDMA resins.

5.5 Conclusions:

Acrylic based cation exchange resins exist commercially, where the exchanging functional group is H^+ . In this chapter we report PMMA-EDMA anion exchange resin which is prepared by gas phase nitration followed by its reduction to amine groups. This weak based resin has an exchange capacity which is about five times the value for commercially available resin.

On further modification with epichlorohydrin, it is found that only one molecule reacts with an amine site and the exchange capacity of the resin goes down to almost half its value. However, on modification with dichloroethane, once again, only

one molecule reacts with a given amine site and its exchange capacity increases by almost 15%. The difference in this behaviour is attributed to the solvation ability of the resultant resin.

In order to assess the solvation ability of the resin, simple experiment were devised to determine the total moisture content as well as shell 1, 2 and 3 moisture contents. As the duration of nitration increases, shell 1 as well as shell 2 moisture content first rise but after 5 hours, they both fall sharply to reach a lower asymptotic value. As against this, the shell 3 moisture content increases steadily and reaches an high asymptotic value for large duration of nitration. On comparison of this resin with the chloroethylated PS-DVB resin, we find that the latter was more hydrophilic in nature.

Table 5.1
Capacity of Epichlorohydrin Modified PMMA-EDMA Resin

Duration of Nitration (hr)	Gravimetric Estimation			Average Capacity (meq/g)	Titration		
	Amount of Resin (g)	Weight of ppt. For two consecutive runs (g)	Capacity (meq/g)		Amount of Resin (g)	Titre values (ml)	Capacity (mmoles/g)
1	0.3219	(i) 0.0262 (ii) 0.0291	0.567 0.631	0.599	0.7963	4.4	0.761
2	0.6592	(i) 0.912 (ii) 0.0794	0.964 0.839	0.902	0.2849	4.7	1.094
3	0.6067	(i) 0.1230 (ii) 0.1053	1.1413 1.209	1.311	0.7336	3.9	1.472
4	0.9631	(i) 0.2710 (ii) 0.2476	1.961 1.792	1.877	0.3917	4.4	1.539
5	0.5347	(i) 0.1639 (ii) 0.1758	2.136 2.291	2.214	0.7270	3.6	1.965
6	0.3649	(i) 0.1579 (ii) 0.1472	3.017 2.812	2.913	0.4619	3.8	2.542
7	0.7854	(i) 0.3283 (ii) 0.3349	2.913 2.972	2.943	0.7664	2.8	2.859
8	0.8380	(i) 0.3296 (ii) 0.3526	2.743 2.921	2.832	0.7401	3.1	2.569
9	0.4886	(i) 0.1685 (ii) 0.1903	2.403 2.714	2.559	0.4393	3.8	2.750
10	0.9238	(i) 0.3504 (ii) 0.3644	2.643 2.749	2.696	0.4579	3.8	2.692
11	0.7261	(i) 0.2119 (ii) 0.2949	2.034 2.830	2.432	0.3460	4.1	2.711
12	0.8229	(i) 0.3029 (ii) 0.2776	2.565 2.351	2.458	0.3160	4.2	2.536

Table 5.2
Capacity of PMMA-EDMA Resins Modified by Trimethylamine

Hours of Nitration (hr)	Amount of Resin (g)	Wt. of ppt. For two consec. Runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of Resin (g)	Titre Value (ml)	Capacity (mmoles/g)
1	0.7435	(i) 0.1126 (ii) 0.1239	(i) 1.05 (ii) 1.16	1.11	0.7555	4.0	1.32
2	0.7076	(i) 0.2572 (ii) 0.2463	(i) 2.54 (ii) 2.43	2.49	0.7077	4.1	1.27
3	0.8413	(i) 0.3417 (ii) 0.3285	(i) 2.84 (ii) 2.73	2.79	0.8488	3.8	1.41
4	0.7183	(i) 0.2660 (ii) 0.2711	(i) 2.58 (ii) 2.63	2.11	0.7065	3.8	1.70
5	0.6193	(i) 0.2408 (ii) 0.2470	(i) 2.72 (ii) 2.78	2.75	0.6263	3.9	1.76
6	0.6202	(i) 0.2886 (ii) 0.2847	(i) 3.25 (ii) 3.21	3.23	0.6273	3.1	3.02
7	0.6831	(i) 0.3099 (ii) 0.2933	(i) 3.17 (ii) 3.05	3.11	0.6917	3.4	2.31
8	0.7635	(i) 0.3461 (ii) 0.3316	(i) 3.17 (ii) 3.03	3.10	0.7649	3.4	2.09
9	0.6762	(i) 0.2980 (ii) 0.2971	(i) 3.08 (ii) 3.07	3.08	0.6662	3.3	2.55
10	0.7240	(i) 0.3560 (ii) 0.3357	(i) 3.43 (ii) 3.24	3.34	0.7315	3.2	2.46
11	0.8621	(i) 0.3150 (ii) 0.3042	(i) 2.55 (ii) 2.46	2.51	0.8257	3.4	1.93
12	1/2000	(i) 0.2984 (ii) 0.3195	(i) 1.73 (ii) 1.86	1.80	1.0500	3.9	1.04

Table 5.3
Capacity of PMMA-EDMA resins Modified by Triethylamine

Hours of Nitration	Amount of Resin (g)	Wt. of ppt. For two concs. Runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of Resin (g)	Titre Value (ml)	Capacity (mmoles/g)
1	0.6868	(i) 0.1337 (ii) 0.1324	(i) 1.36 (ii) 1.34	1.35	0.6913	4.3	1.01
2	0.7074	(i) 0.2300 (ii) 0.2491	(i) 2.27 (ii) 2.46	2.37	0.7025	3.8	1.70
3	1.3042	(i) 0.3409 (ii) 0.3422	(iii) 2.30 (iv) 2.31	2.31	1.0430	3.2	1.72
4	0.7031	(i) 0.3258 (ii) 0.3793	(i) 3.24 (ii) 3.77	3.51	0.7005	3.1	2.71
5	0.6366	(i) 0.3418 (ii) 0.3758	(i) 3.75 (ii) 4.12	3.94	0.6251	3.1	3.03
6	0.7097	(i) 0.2854 (ii) 0.3488	(i) 2.81 (ii) 3.43	3.12	0.7246	3.5	2.07
7	0.6555	(i) 0.4029 (ii) 0.4142	(i) 4.29 (ii) 4.41	3.32	0.7047	3.1	2.69
8	0.7159	(i) 0.3300 (ii) 0.3492	(i) 3.22 (ii) 3.41	3.32	0.7190	3.3	2.36
9	0.7093	(i) 0.3378 (ii) 0.3613	(i) 3.33 (ii) 3.56	3.45	0.7079	3.2	2.54
10	0.6585	(i) 0.3214 (ii) 0.3326	(i) 3.41 (ii) 3.53	3.47	0.6943	3.4	2.30
11	0.6568	(i) 0.3078 (ii) 0.2924	(i) 3.28 (ii) 3.11	3.20	0.6420	3.6	2.18
12	0.6078	(i) 0.3109 (ii) 0.2984	(i) 3.57 (ii) 3.43	3.50	0.5892	3.7	2.21

Table 5.4
Capacity of PMMA-EDMA Resins Modified by Triphenylphosphine

Duration of Nitration (hr)	Amount of Resin (g)	Gravimetric Estimation			Titration		
		Weight of ppt. For two consecutive runs (g)	Capacity (meq/g)	Average Capacity (meq/g)	Amount of Resin (g)	Titre values (ml)	Capacity (mmoles/g)
1	0.7509	(i) 0.2379 (ii) 0.2241	(i) 2.22 (ii) 2.08	2.15	0.7889	3.7	1.69
2	0.7555		(i) 3.42 (ii) 3.26	3.34	0.8178	3.3	2.07
3	0.8544	(i) 0.3646 (ii) 0.3844	(i) 2.98 (ii) 3.15	3.07	0.9215	3.2	1.95
4	0.7242	(i) 0.3909 (ii) 0.3978	(i) 3.77 (ii) 3.84	3.81	0.7168	3.3	2.37
5	0.6961	(i) 0.3614 (ii) 0.3394	(i) 3.63 (ii) 3.41	3.52	0.6905	3.5	2.17
6	0.8249	(i) 0.4973 (ii) 0.4936	(i) 4.22 (ii) 4.18	4.20	0.8172	2.8	2.69
7	0.9596	(i) 0.3843 (ii) 0.4055	(i) 2.80 (ii) 2.95	2.88	0.9448	3.2	1.91
8	0.7445	(i) 0.4217 (ii) 0.4169	(i) 3.96 (ii) 3.92	3.93	0.7415	3.3	2.29
9	0.6706	(i) 0.3489 (ii) 0.3594	(i) 3.21 (ii) 3.30	3.26	0.7622	3.5	1.97
10	0.7570	(i) 0.4332 (ii) 0.4309	(i) 4.00 (ii) 3.98	3.99	0.8115	3.1	2.34
11	0.6529	(i) 0.3089 (ii) 0.3112	(i) 3.31 (ii) 3.33	3.32	0.7062	3.3	2.40
12	0.5722	(i) 0.2180 (ii) 0.2163	(i) 2.66 (ii) 2.64	2.65	0.5813	4.0	1.72

Table 5.5
Equilibrium Water Content of Aminated PMMA-EDMA Resin

Duration of Nitration (hr)	Dry weight of Aminated Resin (g)	Wet Weight of Aminated Resin (g)	Oven dried weight (g)	Vacuum dried weight (g)	Weight after three months	Shell 1 Moisture (2) – (3)		Shell 2 Moisture (3) – (4)		Shell 3 Moisture (4) – (1)	
						g	%	g	%	g	%
	(1)	(2)	(3)	(4)							
0	1.0391	1.1741	1.0769	-	-	0.0972	9.35	-	-	-	-
1	1.1136	1.4891	1.2576	1.2492	1.2138	0.2315	20.79	0.0084	0.75	0.1356	12.18
2	1.1289	1.8709	1.3482	1.3340	1.1466	0.5227	46.31	0.0142	1.25	0.2051	18.17
3	1.8938	3.2184	2.3938	2.2890	1.9037	0.9246	48.82	0.0048	0.25	0.3952	20.87
4	1.2759	2.0767	1.6077	1.5918	1.2968	0.4690	36.76	0.0159	1.25	0.3159	24.76
5	1.6837	3.0170	2.1691	2.1437	1.6993	0.8479	50.36	0.0254	1.51	0.4600	27.32
6	1.4932	2.7625	1.0178	1.9383	1.5197	0.7447	49.87	0.0795	5.32	0.4451	29.81
7	1.4008	2.5364	1.8930	1.8022	1.4131	0.6434	45.93	0.0908	6.48	0.4014	28.66
8	1.3976	2.4854	1.8193	1.8156	1.4018	0.6661	47.66	0.0037	0.26	0.4180	29.91
9	1.4931	3.3642	1.7817	1.7739	1.5138	0.5825	39.01	0.0078	0.52	0.2808	18.81
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

- Dry weight of the samples were taken after six months storage on December 1998. (The samples were placed in the dessicator on July 1998).

* Percentage calculations has been determined on the basis of dry weight given in column 1.

Table 5.6
Equilibrium Water Content of Trimethylamine Modified PMMA-EDMA Resin

Duration of Nitration (hr)	Dry weight of Aminated Resin (g)	Wet Weight of Aminated Resin (g)	Oven dried weight (g)	Vacuum dried weight (g)	Weight after three months	Shell 1 Moisture (2) – (3)		Shell 2 Moisture (3) – (4)		Shell 3 Moisture (4) – (1)	
	(1)	(2)	(3)	(4)		g	%	g	%	g	%
0	1.0391	1.1741	1.0769	-	-	0.0972	9.35	-	-	-	-
1	1.1278	1.4824	1.2976	1.2446	1.2517	0.1848	16.39	0.0530	0.045	0.1168	10.36
2	1.3612	1.9121	1.5695	1.5544	1.5603	0.3426	25.17	0.0151	0.011	0.1932	14.19
3	1.1051	1.7101	1.3092	1.2960	1.3029	0.4009	36.28	0.0131	1.19	0.1909	17.27
4	1.4938	2.4250	1.8076	1.7954	1.8018	0.6174	41.33	0.0122	0.82	0.3016	20.19
5	1.3702	2.3486	1.7294	1.7239	1.7391	0.6192	45.19	0.005	0.40	0.3537	25.81
6	1.1174	2.0389	1.4605	1.4485	1.4599	0.5784	51.77	0.012	1.07	0.3311	29.63
7	1.7600	3.1641	2.2819	2.2723	2.2801	0.8822	450.13	0.009	0.56	0.5123	29.11
8	12.869	2.3064	1.6654	1.6502	1.6618	0.6410	49.81	0.0152	1.18	0.3633	28.23
9	1.3015	2.3356	1.6882	1.6753	1.6873	0.6474	49.74	0.0129	0.99	0.3738	28.72
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

- Dry weight of the samples were taken after six months storage on December 1998. (The samples were placed in the dessicator on July 1998).

* Percentage calculations has been determined on the basis of dry weight given in column 1.

Table 5.7
Equilibrium Water Content of TEA Modified PMMA-EDMA Resin

Duration of Nitration (hr)	Dry weight of Resin (g)	Wet Weight of Resin (g)	Oven dried weight (g)	Vacuum dried weight (g)	Weight after three months	Shell 1 Moisture (2) - (3)		Shell 2 Moisture (3) - (4)		Shell 3 Moisture (4) - (1)	
	(1)		(3)	(4)		g	%	g	%	g	%
0	1.0391	41	1.0769	-	-	0.0972	9.35	-	-	-	-
1	1.4632	92	1.6847	1.6738	1.4716	0.1655	11.31	0.0109	0.75	0.2106	14.39
2	1.4410	93	1.6999	1.6880	1.4539	0.3094	21.47	0.0119	0.83	0.2470	17.14
3	1.5979	93	1.0276	1.9314	1.6028	0.4017	25.14	0.0862	5.39	0.3335	20.87
4	1.4000	2.2968	1.8124	1.7175	1.5101	0.4844	34.60	0.949	6.78	0.3175	22.68
5	1.3726	2.3117	1.7327	1.7215	1.3918	0.5790	42.18	0.0112	0.81	0.3489	25.42
6	1.1380	2.0602	1.4598	1.4454	1.2409	0.6004	52.76	0.0144	1.26	0.3074	27.01
7	1.2974	2.3935	1.6904	1.6778	1.3017	0.7031	54.19	0.0126	0.97	0.3804	29.32
8	1.5188	2.9197	2.1038	2.0024	1.5298	0.8159	53.72	0.1014	6.67	0.4836	31.84
9	1.6724	3.0961	2.2101	2.1938	1.6845	0.9023	52.98	0.0163	0.98	0.5214	31.17
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

- Dry weight of the samples were taken after six months storage on December 1998. (The samples were placed in the dessicator on July 1998).

* Percentage calculations has been determined on the basis of dry weight given in column 1.

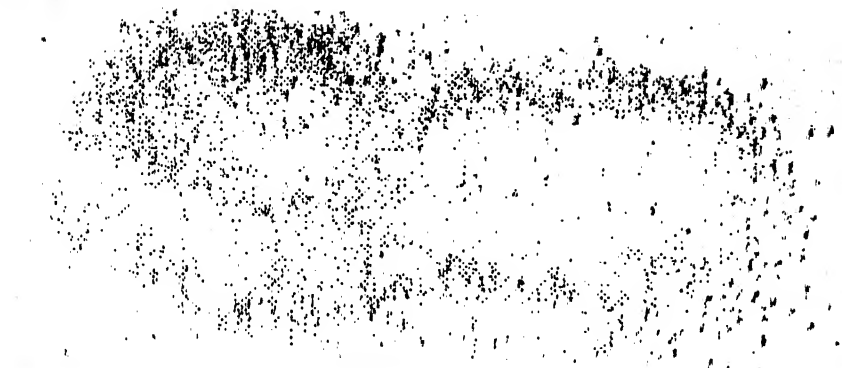
Table 5.8
Equilibrium Water Content of TPP Modified PMMA-EDMA Resin

Duration of Nitration (hr)	Dry weight Of resin (g)	Wet Weight of resin (g)	Oven dried weight (g)	Vacuum dried weight (g)	Weight after three months	Shell 1 Moisture (2) – (3)		Shell 2 Moisture (3) – (4)		Shell 3 Moisture (4) – (1)	
						g	%	g	%	g	%
	(1)	(2)	(3)	(4)							
0	1.0391	1.1741	1.0769	-	-	0.0972	9.35	-	-	-	-
1	1.3130	1.7401	1.5518	1.5294	1.3279	0.1883	14.34	0.0224	1.70	0.2164	16.48
2	1.4769	2.1324	1.7899	1.7795	1.4817	0.3425	23.19	0.0104	0.704	0.3026	20.49
3	1.1965	1.8370	1.5203	1.5071	1.2038	0.3167	26.47	0.0132	1.10	0.3106	25.96
4	1.2427	1.9859	1.6109	1.5977	1.2517	0.3750	30.18	0.0132	1.06	0.3550	28.57
5	1.4952	2.4887	1.9594	1.9439	1.4859	0.5293	35.40	0.0155	1.03	0.4487	30.01
6	1.1104	1.9179	1.4718	1.4577	1.1296	0.44612	40.18	0.0141	1.26	0.3473	31.28
7	1.6810	3.111	2.2411	2.2313	1.6998	0.8700	51.76	0.0098	0.58	0.5503	32.74
8	1.2981	2.4592	1.7390	1.7279	1.3018	0.7202	55.48	0.0111	0.85	0.4298	33.11
9	1.3456	2.5830	1.8200	1.8084	1.3579	0.7630	56.70	0.0116	0.86	0.4628	34.39
Dowex	0.997	1.761	1.563	1.001	1.038	0.198	19.9	0.562	46.36	0.004	0.04

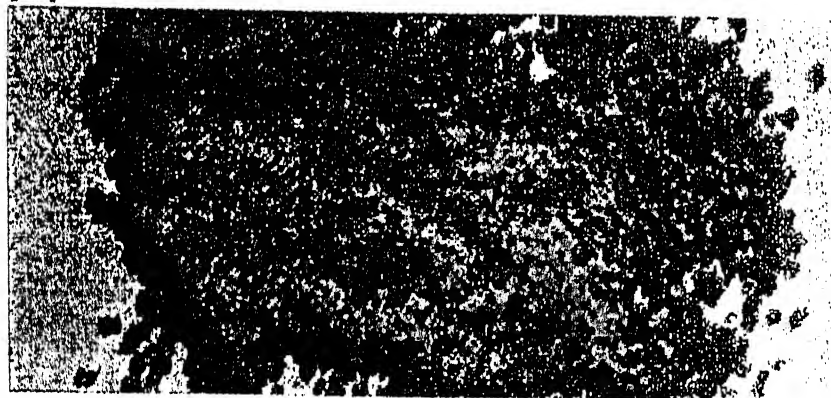
- Dry weight of the samples were taken after six months storage on December 1998. (The samples were placed in the dessicator on July 1998).

* Percentage calculations has been determined on the basis of dry weight given in column 1.

(a)



(b)



(c)



(d)



Figure 5.1 : Effect of modification on colour of PMMA-EDMA resin

(a) Unmodified, (b) Surface Nitrated, (c) Surface Aminated

(d) Epichlorohydrin reacted

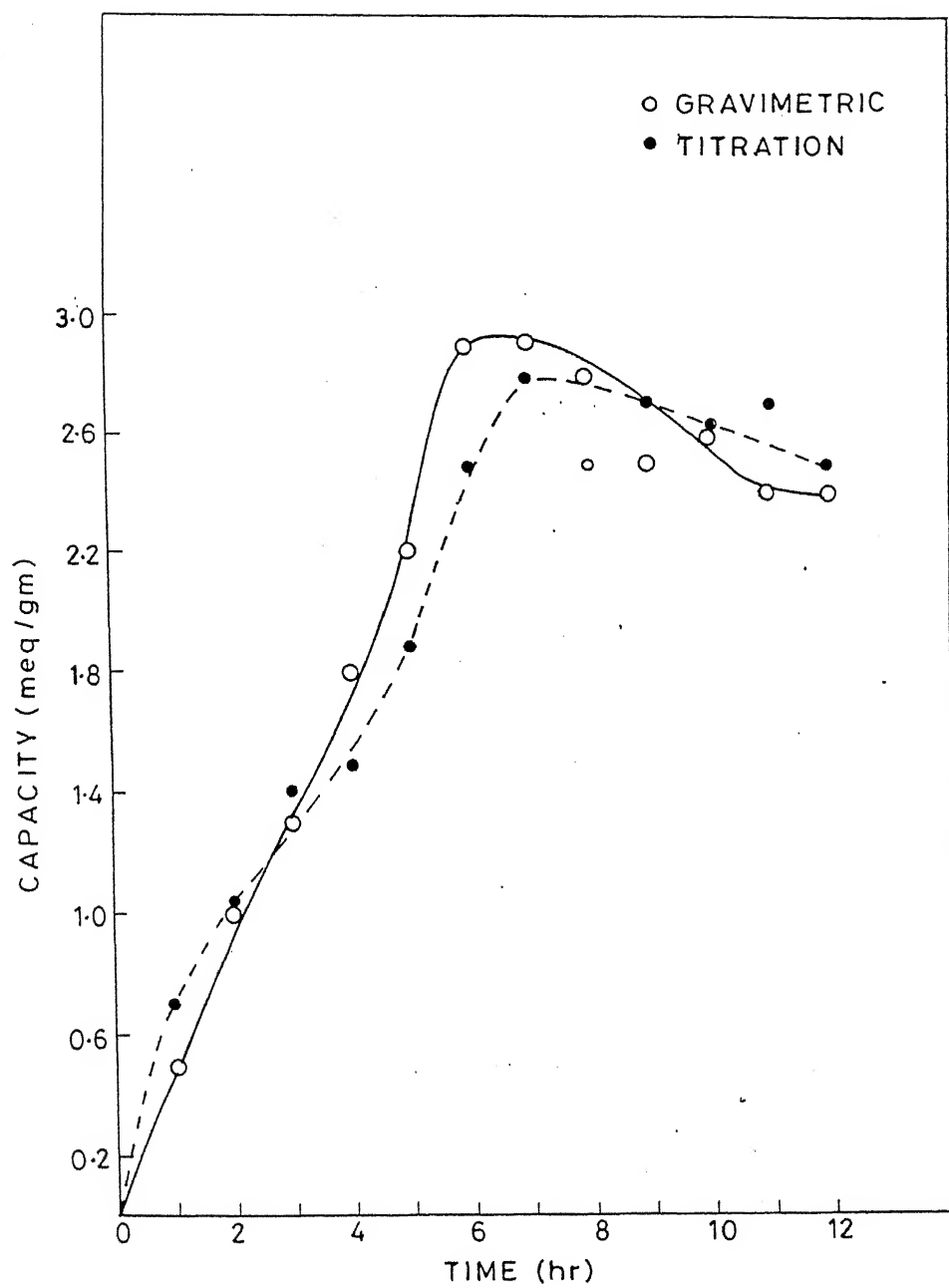


Figure 5.2 : Effect of Nitration Time on Epichlorohydrin Modified PMMA-EDMA Resin

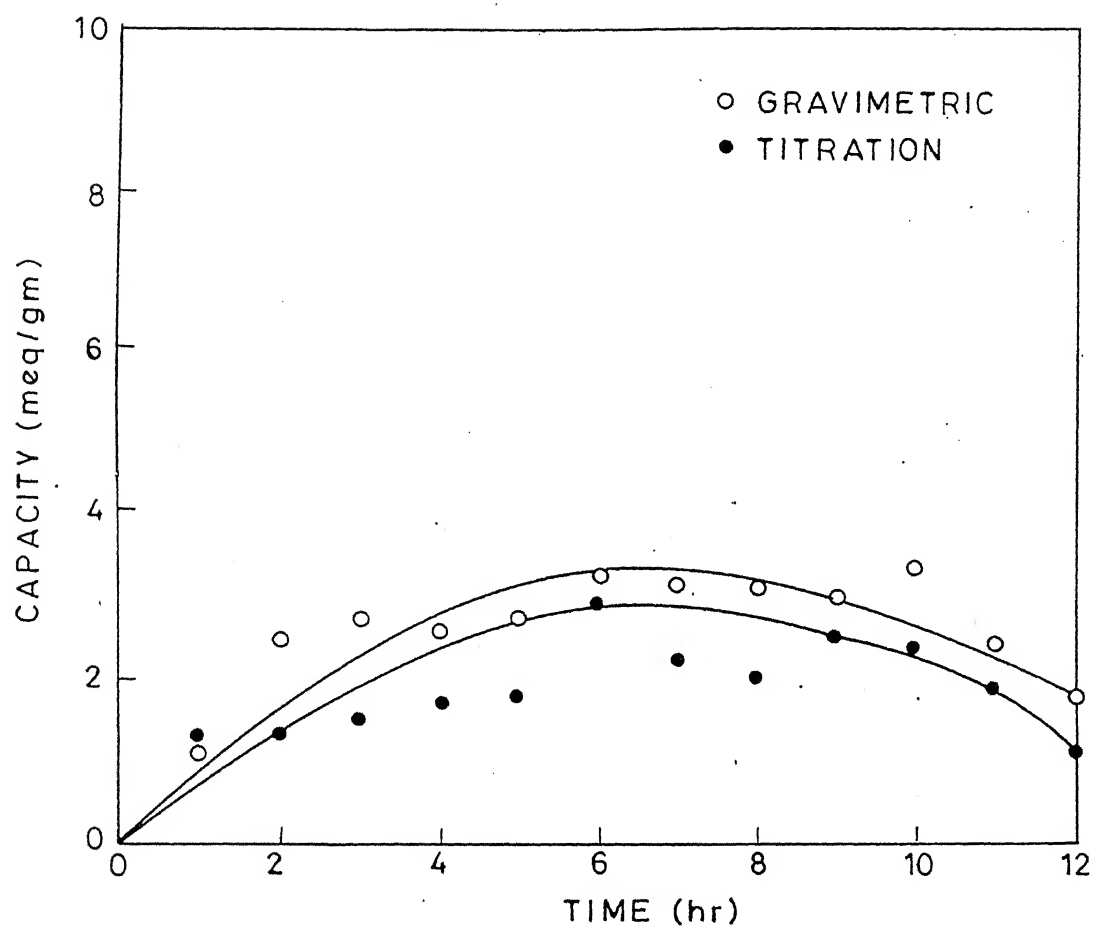


Figure 5.3 : Effect of Nitration Time on the Capacity of PMMA-EDMA Resin Modified by Trimethylamine

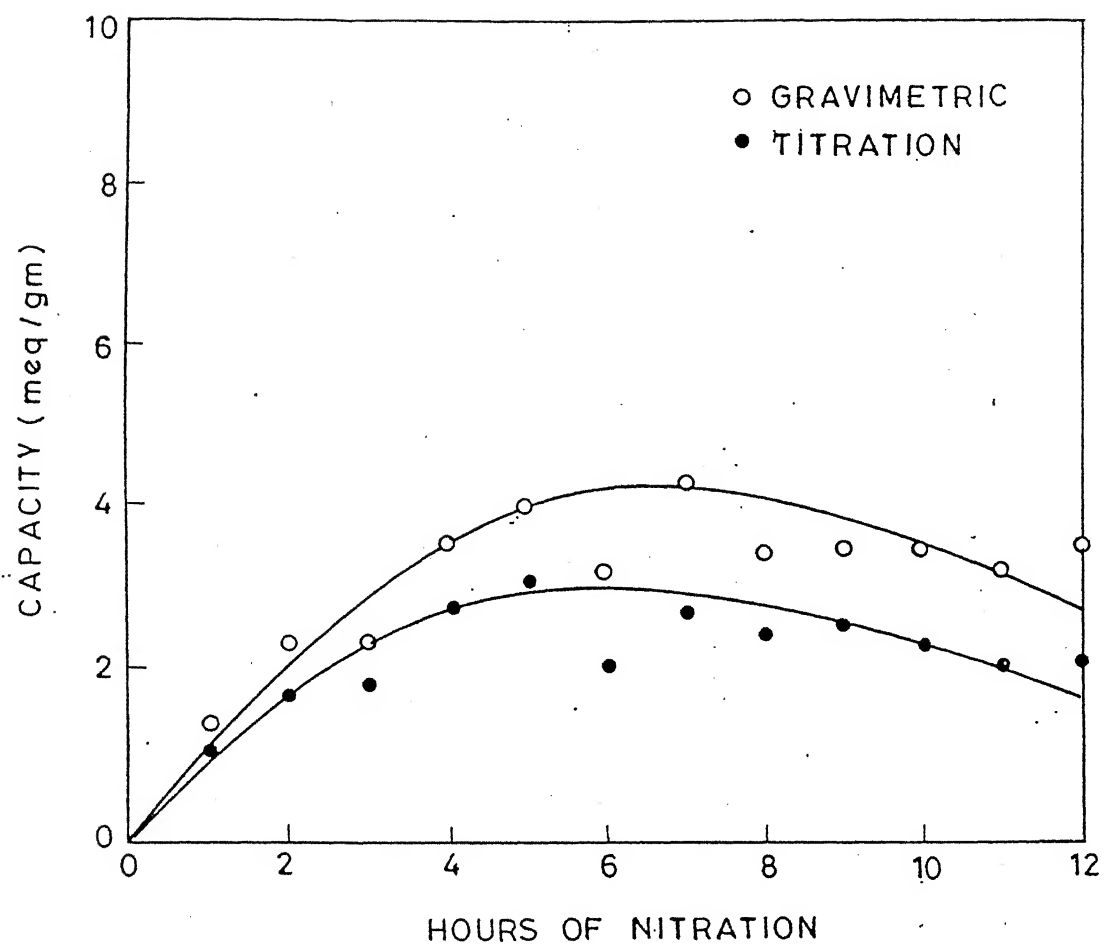


Figure 5.4 : Effect of Nitration Time on the Capacity of PMMA-EDMA Resin Modified by Triethylamine

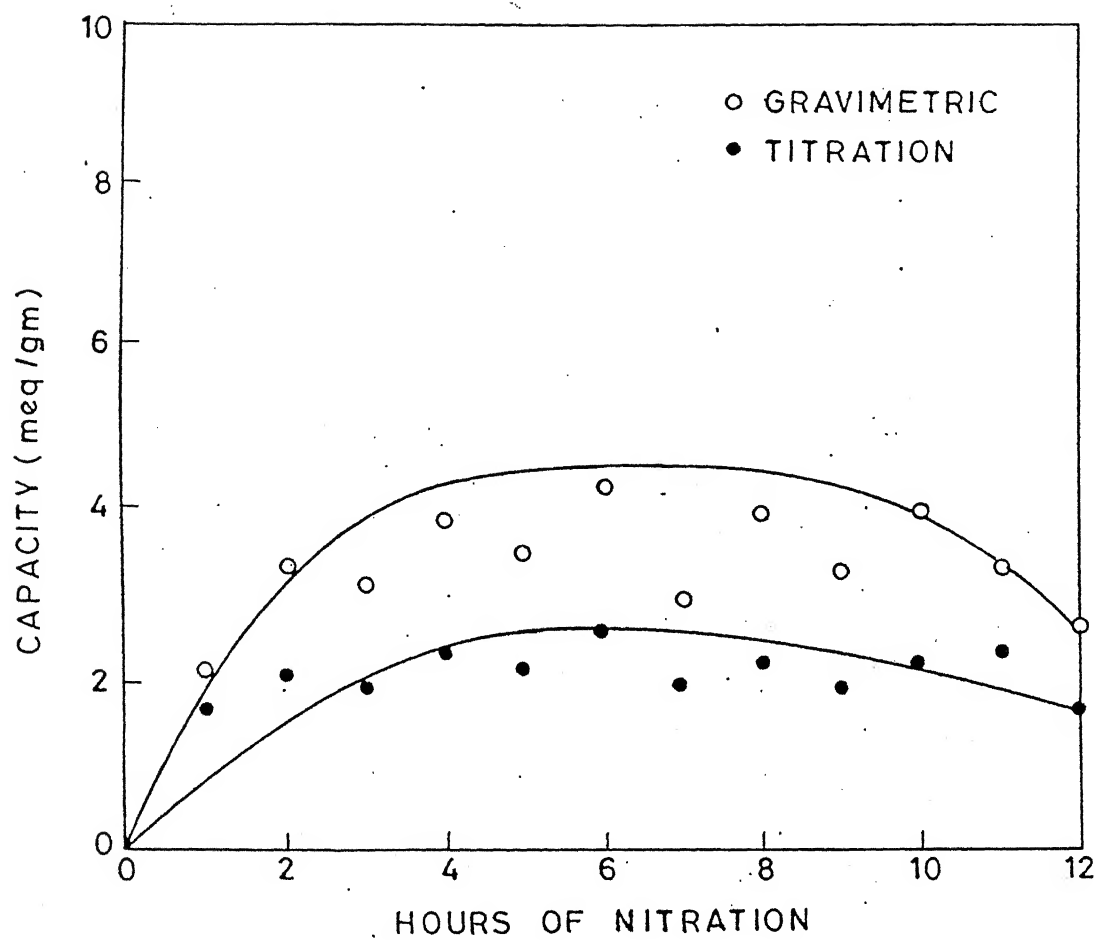


Figure 5.5 : Effect of Nitration Time on the Capacity of PMMA-EDMA Resin Modified by Triphenylphosphine

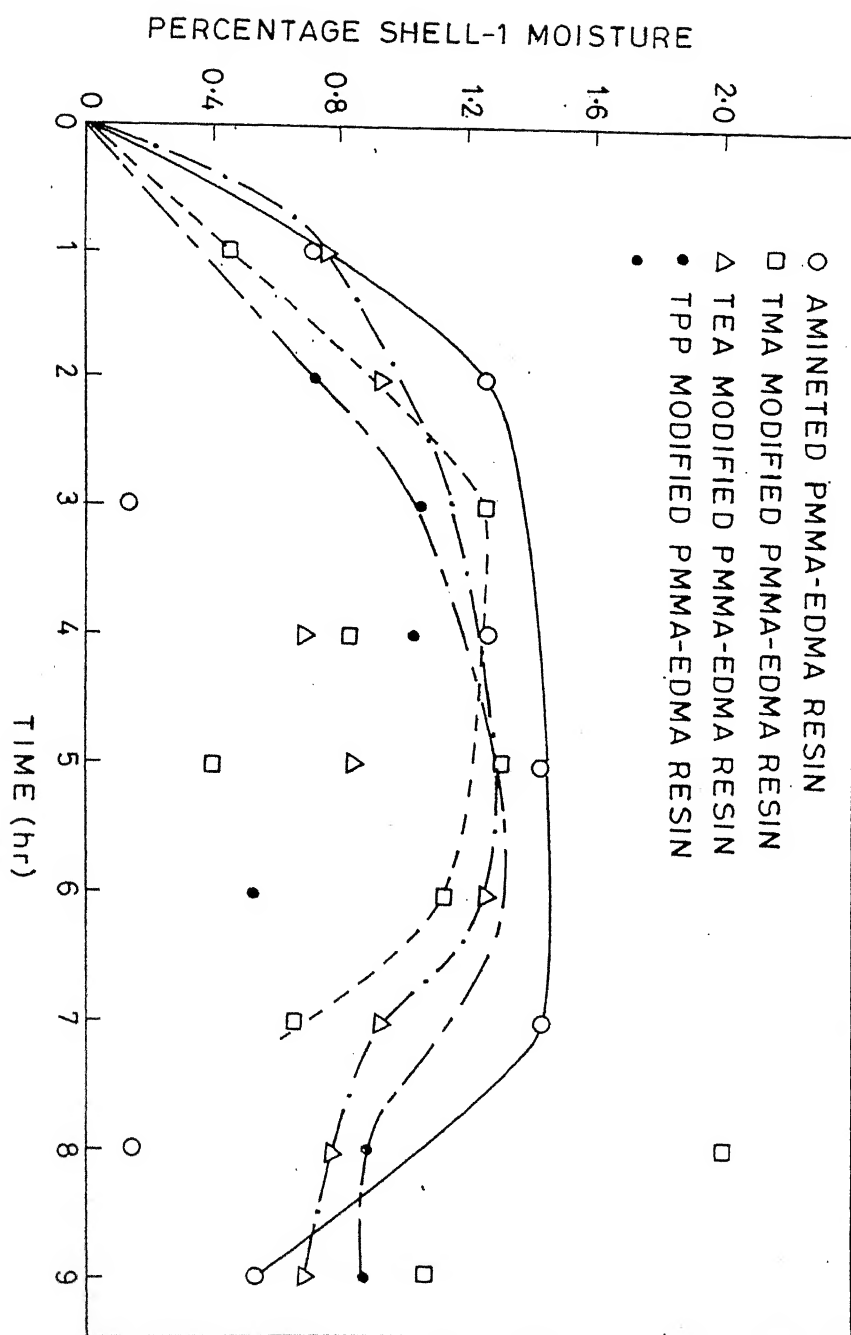


Figure 5.6 : Shell 1 Moisture Content of PMMA-EDMA Resins

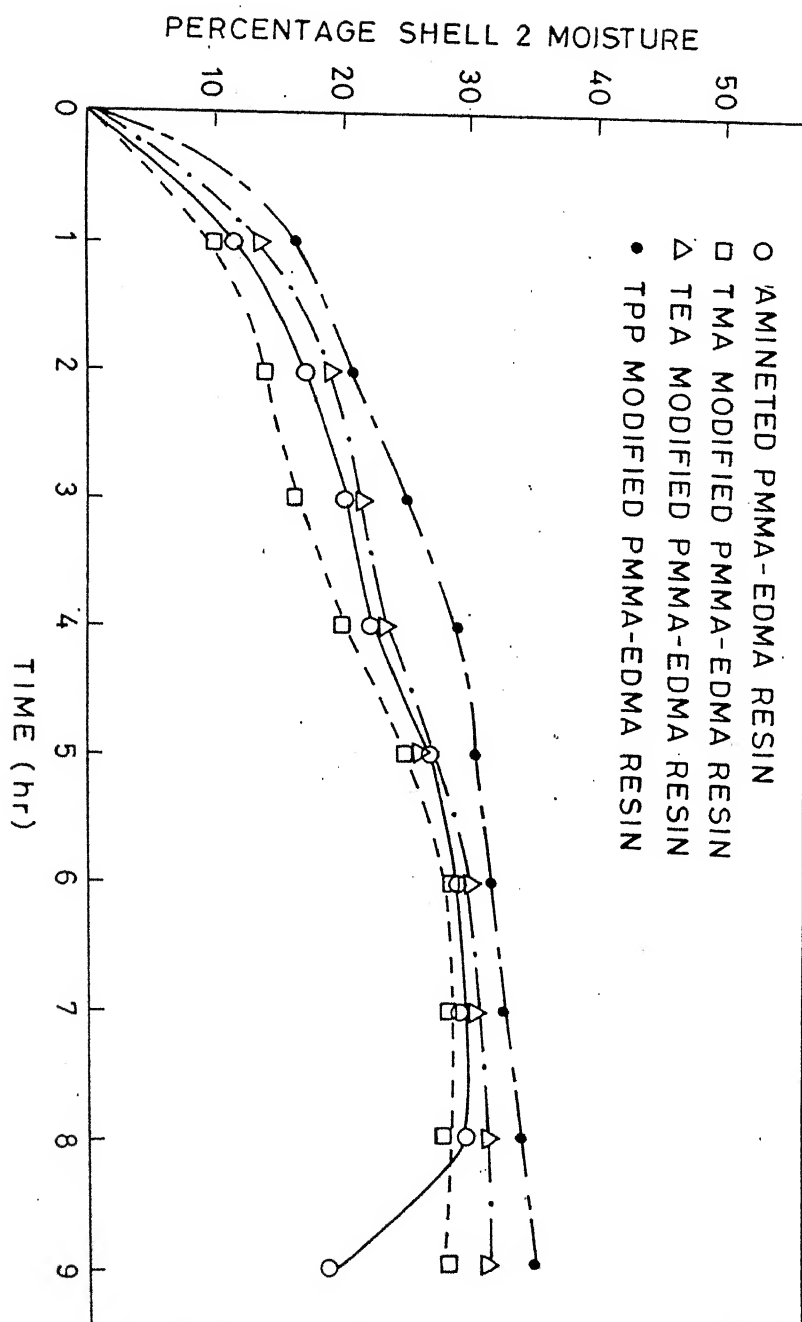


Figure 5.7 : Shell 2 Moisture Content of PMMA-EDMA Resins

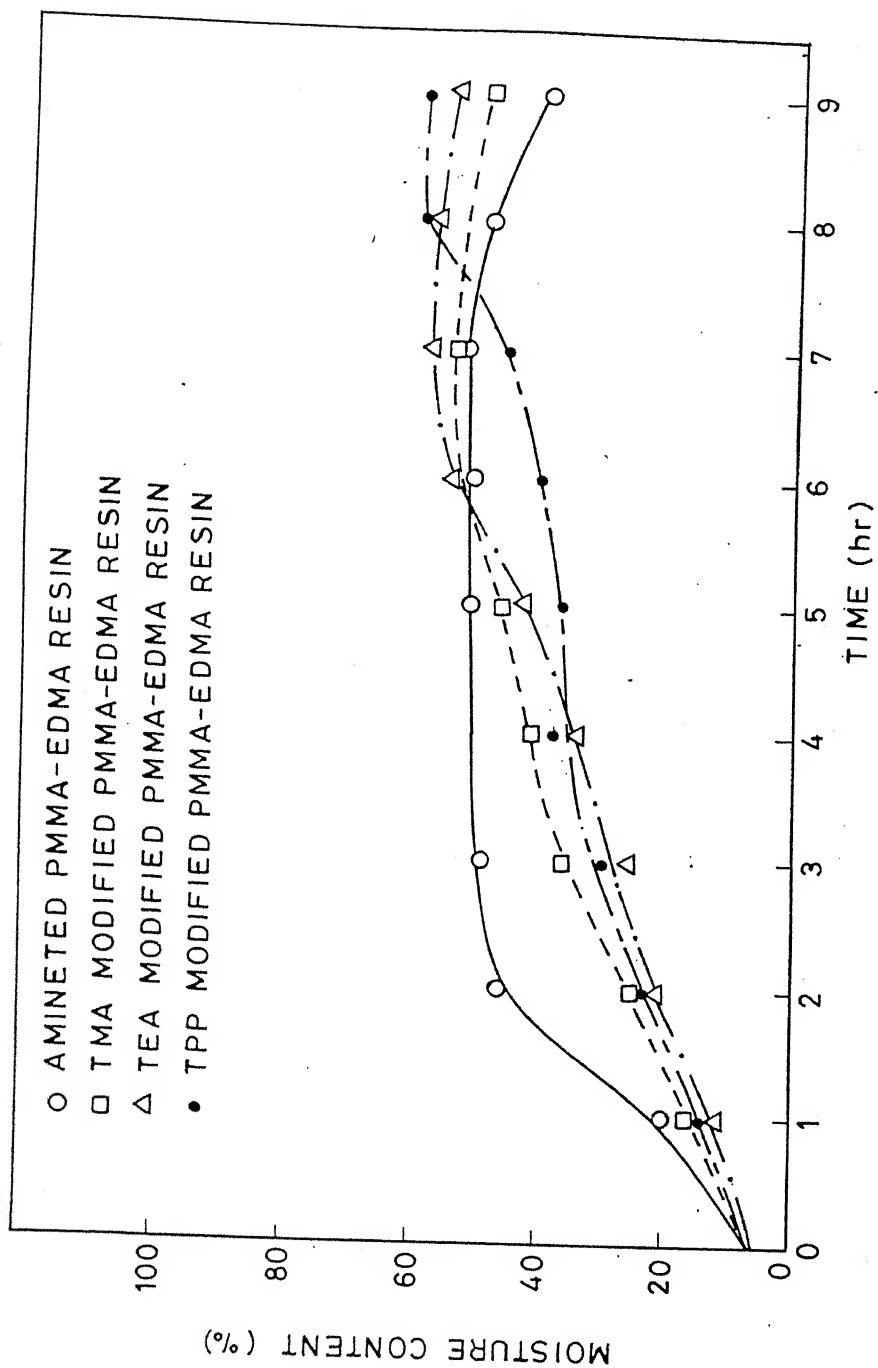


Figure 5.8 : Shell 3 Moisture Content of PMMA-EDMA Resins

FUTURE PLAN OF WORK

The nitration technique developed during this study is found to be very effective. Major portion of the cost of polymer based ion exchange resin (anionic or cationic) is the cost of crosslinked polymer and it is desired to find a cheaper substitute for this material. This technique of nitration using NO_x can be applied on cheap and naturally available supports like silica gel, quartz sand, coal etc. for modification of their matrix and generation of amine functional groups. We have confirmed the occurrence of this reaction on these materials. However this technique does not work on material cellulose materials like wood, cotton etc. very well because of degradation of these materials instead of nitration. It is also ineffective over the metals where metal oxides are formed.

In this study we have applied this method of nitration to macroporous polymeric material only. There are plenty of macroporous and isoporous ceramic materials and gellular polymers. The application of this technique may further be extended to these materials for the preparation of ion exchangers. We have only discussed the macriporous polymeric materials developed in the work for usage in separation technology. These materials can be used for a support for metals and their salts in heterogeneous catalysis as follows. This modification technique can be used for functionalization of the support materials so that they can complex with the metal salt this way preventing the leaching of the metal during the catalytic reaction.

In another class this modification scheme has been successfully applied to the glass composites. These modified composite materials, when they are held together by application of suitable adhesives form covalent bond joined more effectively. We have confirmed this experimentally. Therefore this modification scheme can also be applied as

a repair technology modification. In this the functionalization of joints through this improves the performance of joints.

In the aerospace industry the carbon fibre composites are immersed a structural materials. These composites can undergo damage under impact loading. These composites can also adsorbs moisture which may produce delamination of the various piles in it. The current technology requires that these composite plates be removed and replaced. This is because it is not possible to repair due to the inertness of crosslinked epoxy polymer binding. This nitration technique can be used to generate the amine groups on the epoxy polymer and the damaged area can be repaired using butt joints.

So one can observe the wide application of this clean and cheaper technology. This opens a new horizon of research in the field of modification.

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